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INVESTIGATION OF THE ADSORPTION OF VAPORS ON QUARTZ

COMMUNICATION 1. METHOD OF INVESTIGATING ADSORPTION ISOTHERMS

A. I. Sarakhov

In the development of the theory of adsorption, the investigation of adsorption on nonporous adsorbents occupies a particularly important place, since it enables us to reach certain conclusions regarding the interactions of adsorbed molecules among themselves and with the adsorbent surface. In this connection great interest is presented by the study of adsorption on nonporous crystalline adsorbents having a comparatively homogeneous surface of known extent and similar to the surface of industrial adsorbents in chemical composition. However, very few such investigations have been described, a fact that is to be explained by the great difficulties met in the measurement of adsorption on such adsorbents. The specific surfaces of nonporous adsorbents are hundreds of times less than those of the usual adsorbents, so that the sensitivity of the methods used for the investigation of nonporous adsorbents must be hundreds of times as high as that of the usual methods.

In the main, three methods are used at present for the measurement of the adsorption of gases and vapors on solid adsorbents: the volumetric method, the gravimetric method, and the method, recently introduced, of independent weighing [1]. In the general case it is difficult to decide which of these methods is the best, for their accuracy is appreciably dependent on the character of the systems investigated and none of them is altogether universal. However, for the study of the adsorption of vapors of substances of low vapor pressure on nonporous adsorbents the best method would be the gravimetric method if its accuracy could be increased to that of the independent-weighing method or to the highest accuracy that can be obtained in volumetric methods. This could be done by increasing the sensitivity of the balance.

The low accuracy of the gravimetric method is not explicable in general by the low sensitivity of the balance used for the adsorption measurements, but must be attributed to the fact that in the gravimetric method it is necessary to weigh the adsorbed substance together with the adsorbent itself, which is very much heavier than adsorbed substance and forms an undesirable ballast in the weighing. For adsorption on nonporous adsorbents the ratio of the weights of adsorbent and adsorbed substance may be 1000 : 1 or higher for medium values of adsorption. If it is required that the accuracy of the method shall not be lower than that of other modern methods, the relative sensitivity of the balance—i.e. the ratio of absolute sensitivity to maximum load—must be about $1 \cdot 10^{-7}$. It should be noted that the relative sensitivity of the sorption balance generally used is about $1 \cdot 10^{-4}$ [1].

In general, balances having a relative sensitivity of $1 \cdot 10^{-7}$ are not rare, for as early as 1895 Mendeleev [2] worked with a balance of sensitivity $1 \cdot 10^{-9}$, and balances of sensitivity $1 \cdot 10^{-9}$ or thereabouts are now to be found in many laboratories. Unfortunately, the specificity of adsorption measurements completely excludes the possibility of using standard commercial balances for this purpose. Consequently, every investigator that selects the gravimetric method of measuring adsorption must himself construct, and often design, a balance that will meet his requirements.

Dozens of microbalances of different designs have been described in the literature (see, for example, the review articles [3-5]). These were designed for a great variety of purposes, including adsorption measurements. A critical examination of more than fifty papers describing balances of different designes showed that the most suitable balance for the investigation of adsorption on nonporous adsorbents is that of Gulbransen [6, 7], as improved by Rhodin [8]. Even this balance, however, has a somewhat low relative sensitivity, and it has some defects in design. It must be pointed out that almost all of the balances described were constructed without making the appropriate theoretical analysis and calculations.

The above considerations led us to set ourselves the following problem: to design and construct an adsorption balance having a relative sensitivity of about $1 \cdot 10^{-7}$ at a load of 1 g, the maximum change in the weight of the adsorbent due to adsorption being about 2 mg. The design was based on that of the torsion-beam microbalance.

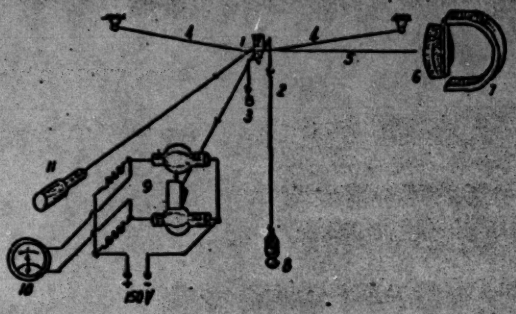

Fig. 1. Diagram showing principle of the balance.

When the precise design had been decided, detailed calculations were made for the balance: a general equation was obtained for the sensitivity of a balance of this type, and all factors affecting the sensitivity were evaluated. The scheme of the balance is shown in Fig. 1. The short beam 1 (shoulder length 1 cm), made from fused quartz rods, is supported by two quartz threads 4 (each length 10 cm and diameter about 25 μ), which are almost horizontal and ensure that the beam will oscillate about its horizontal axis (they are analogous to the central prism in the analytical balance). At the ends of the beam the quartz threads 2 (diameter about 8 μ) are fused; they act as suspensions for cups containing adsorbent (8) and its counterpoise (3). When one of the supporting threads 4 is fused to the beam, a second thread 5 is fused on at the same time, and this serves as a torsion thread, its other end being fused to the axle of the graduated dial 6. The torsion thread is 15 cm in length and about 15 μ in diameter. An iron plate is rigidly attached to the graduated dial 6 so that the dial can be rotated with the magnet 7, which is placed outside the glass balance case.

We shall examine the working of the balance. Let us assume that the beam is first approximately balanced in the horizontal position by the selection of a counterpoise that is correct within 0.1 mg. With the aid of the magnet 7 the beam is then brought exactly into the "zero position", determined optically by means of a mirror attached to the beam; the optical arrangement will be described in detail below. The torsion angle of the torsion thread corresponding to the initial weight of the adsorbent is read on the dial 6, which is graduated in 1° intervals. Any subsequent change in the weight of the adsorbent – resulting from adsorption or desorption – causes the beam to be deflected from its zero position. This deflection is nullified by twisting the torsion thread, the torsion angle being proportional to the extent of adsorption or desorption. The torsion thread used permits twisting for 15 turns in each direction. The number of complete turns of the thread are read from a revolution counter attached to the magnet 7 (not shown in the figure).

The separation of the functions of the supporting and torsion threads enabled us to increase the robustness of the balance appreciably and to increase the permissible change in weight of the sample during the experiment. Otherwise, the total tension in the thread may attain 60-80 kg / sq.mm, which, although permissible for quartz threads of this diameter, is already close to the limiting value; accidental jolts during loading or weighing can easily break the balance.

Calculation showed that, in order to obtain the required sensitivity in a balance of this design, the zero position must be established accurate within $1 \cdot 10^{-8}$ radian. It is well known how difficult it is to obtain such a sensitivity by the measurement of small angles by the usual optical methods, for example, the mirror and scale method. In the present case the use of such methods is excluded since the nonuniform thickness of the evacuated glass balance case makes it impossible to observe the scale, and the incorporation of an optically plane glass window into the case would make the construction of the case extremely difficult. These difficulties were overcome by the use of an optical system that included photocells; the principle of the system is shown in Fig. 1.

A slightly divergent beam of light from a source and slit 11 falls on the balance mirror and is reflected through a lens (not shown on Fig. 1), which focuses an image of the slit, reduced in size, on the edge of a prism. The prism divides the beam of light into two parts, which fall on two photocells contained in the bridge circuit 9. When the beam is deflected, the light falling on the photocells is redistributed and the bridge is thrown out of balance, which is indicated by the reading of the galvanometer 10 in the diagonal of the bridge. It should be noted

that this arrangement, which enables small angles of the order of $1 \cdot 10^{-5}$ radian to be read directly with comparative ease, has a further very valuable property, namely: it enables small angles to be measured with the same accuracy even when the mirror is oscillating slightly. It is therefore unnecessary to provide special suspensions or foundations for apparatus that is liable to receive jolts from neighboring apparatus and machines, etc.

The balance was calibrated and its sensitivity was determined with the aid of observations on the variations in the buoyancies of two loads of known volume hung on the balance, the measurements being made in dry air. One load, a hollow glass sphere, had a volume of 4.5941 ± 0.0002 cc, the other, a platinum rod, had a volume of 0.0479 ± 0.0002 cc. The volumes of the loads were determined by the method of hydrostatic weighing on an analytical balance. Each load weighed about 1 g. When the pressure in the balance case was changed by 0.01 mm of mercury, the difference in the buoyancies of the two loads changed by about $8 \cdot 10^{-9}$ g; a range of pressures from 0 to 300 mm covered the whole of the working range of the balance. The calibration results showed that there was an excellent linear relationship between the torsion angle of the thread and the weight over the whole of the range investigated. The balance constructed on this principle had a sensitivity of $5.7 \cdot 10^{-8}$ g at a load of 1 g, and the permissible change of weight in the course of the experiment was 2.5 mg. It must be pointed out that the calculated sensitivity of the balance was in close accord with the value obtained experimentally in the calibration.

The calculations required for the design of the balance amounted essentially to the determination of the diameters and lengths of the threads (the supporting, torsion, and suspending threads), and they did not go outside the usual problems on elasticity in their scope. We will mention only that the diameter and length of the torsion thread are determined by the specified maximum change in weight and sensitivity. The absolute sensitivity of the balance can be calculated from the following formula, which we obtained from the conditions for balance of the beam:

$$\Delta P = \left[\frac{G\pi}{32}\left(\frac{d_1^4}{l_1} + \frac{2d_2^4}{l_2}\right) + \sqrt{PE\frac{\pi d_3^4}{64}} + (mb_2 + 2Pb_1)\right]\frac{\varphi}{a}, \qquad (1)$$

in which ΔP is absolute sensitivity; E and G are elasticity moduli of the first and second kinds for quartz; P is the load on the balance; d_1 and l_1 are the diameter and length of the torsion thread; d_2 and l_2 are the diameter and length of the supporting threads; d_3 is the diameter of the threads that suspend the loads; m is the weight of the beam itself; a is the length of the shoulder of the beam; b_1 is the distance between the axis of rotation of the beam and a line drawn between the points at which the tensions in the suspensions are applied to the beam; b_2 is the distance between the axis of rotation of the beam and the center of gravity of the beam itself; φ is the smallest measurable angle of rotation of the beam. In this equation the quantities b_1 and b_2 are very difficult to determine. In the calculation, therefore, it is necessary to assume a value of $(mb_2 + 2Pb_1)\frac{\varphi}{a}$ (which depends on the balancing of the beam) that is several times less than ΔP. The assembled balance must then be loaded with nominal weights, and the final balancing of the beam must be carried out in this condition until the calculated sensitivity is obtained. The value of $(mb_2 + 2Pb_1)\frac{\varphi}{a}$ will then be adjusted to the assumed value.

The general scheme of the apparatus is given in Fig. 2. The balance itself is assembled on a metal framework and is sealed in the balance case A, which is in the form of a sealed glass T-piece. The balance case is contained in an air thermostat T. The ampoule B containing the substance to be absorbed, which is first purified and degassed, is contained in the cryostat C, and before the adsorption measurements are started it is isolated from the balance by the glass membrane P. Before the experiment the whole system is subjected to prolonged evacuation, the balance then being heated to about 70° and the adsorbent to 180° – 400°, depending on its nature. When a vacuum of the order of 10^{-6} mm is attained, the apparatus is sealed off from the vacuum pumps and manometers by fusion of the constriction at D. The diaphragm P is then broken, and the adsorption measurements are begun.

The pressure in the balance case of the vapor to be adsorbed is varied with the aid of a cryostat. For

• The term $\sqrt{PE\frac{\pi d_3^4}{64}}$, which determines the value of the bending moment of the suspending thread (which is rigidly attached to the beam), was obtained by Popov's method [9].

substances for which the relationship between saturated vapor pressure and temperature is known, the pressure of the vapor can be calculated from the temperature of the cryostat. It can also be measured directly, and for this purpose a second ampoule E is placed in the cryostat; this contains the substance under investigation, and it is attached to a McLeod gage M_1 and a U-shaped mercury manometer M_2.

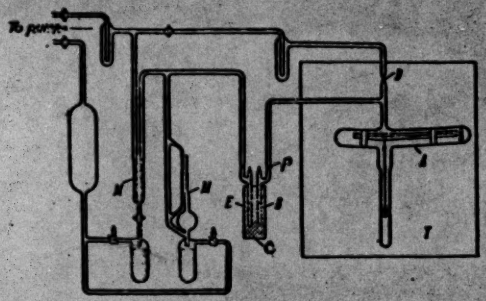

Fig 2 General scheme of adsorption apparatus

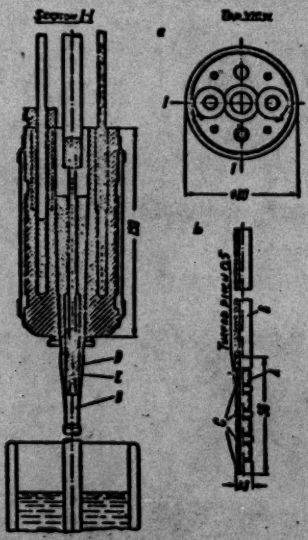

Fig. 3. Construction of cryostat and controlling thermometer.

Such an arrangement was dictated by the necessity for the exclusion of the vapors of mercury and vacuum grease from the space containg the adsorbent, for it was found that the trap containing gold turnings generally used for the absorption of mercury vapor does not give satisfactory protection, and that the adsorption of vapors from vacuum grease is quite appreciable at the given balance sensitivity. Moreover, the presence of vacuum grease limits the choice of substances for adsorption in this apparatus.

We have designed and constructed a special cryostat for use with this apparatus; its construction is shown in Fig. 3. A massive copper block is cooled by a copper rod B, the lower end of which is immersed in liquid nitrogen. We examined the possibility of controlling the temperature of the cryostat roughly and cooling the cryostat rapidly by varying the amount of heat conducted from the block to the liquid nitrogen. With this in view, the upper end D of the rod B was made of synthetic resin of poor thermal conductivity. When the rod is displaced in the vertical direction, there is a change in the area of thermal contact between the copper of the rod B and the conical copper tube E, which is in good thermal contact with the block; the rate at which the block cools changes correspondingly.

The high thermal conductivity of copper enables a fairly uniform temperature to be maintained throughout the block. However, to reduce possible temperature gradients, the block is cooled in its central region and the electric heater is on its outer surface. With the same object in view, the ampoules containing the substance under investigation and the controlling and measuring thermometers are in holes arranged symmetrically in the block with respect to heater and cooler. A 5-cm layer of the porous synthetic resin PS-4 was used as thermal insulation for the block.

The precise control of the temperature of the cryostat is effected automatically, and the temperature can be maintained constant at any value in the range from −150° to + 50°. The automatic thermostating is effected with the aid of a controlling platinum resistance thermometer (Fig. 3c), an electron-tube circuit, and a heater. The platinum thermometer is designed so as to ensure extremely good thermal contact between it and the cryostat block, which appreciably reduces the thermal inertia of the thermometer. The thermometer was made from a platinum wire 50 μ in diameter, which was laid in a thread cut on the copper tube A. The wire was insulated from the copper tube with a layer of polymerized Bakelite. The tube has belts C that are ground to fit the hole in the cryostat block. The thermometer leads are fixed in the tube B, which is made of synthetic resin. The resistance of the thermometer is about 73 ohms at room temperature.

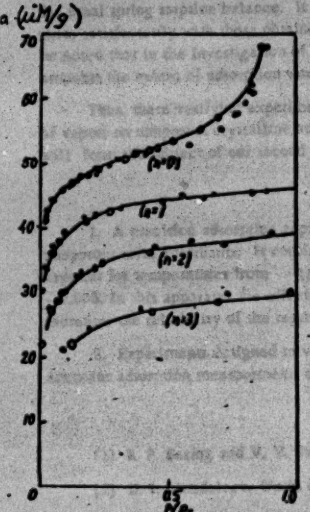

Fig. 4. Adsorption isotherm for methanol vapor on barium sulfate at 25°.

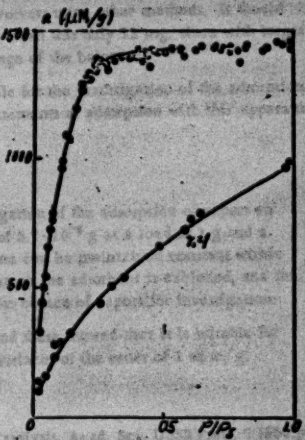

Fig. 5. Adsorption isotherm for heptane vapor on homogeneous finely porous silica gel at 20°

The controlling thermometer forms part of a Wheatstone bridge supplied with 400-cycles 2-v a.c. current from a low-power single-tube generator. The bridge is connected through a transformer to a first-stage amplifier, which is a triple-cascade aperiodic arrangement of 6Zh8 electron tubes with a limited range of emitted frequencies (100 to 800 cycles). The first-stage amplifier is connected through a copper oxide rectifier to a final-stage constant-current amplifier; the anode current of the last electron tube feeds the cryostat heater. The cryostat heater is made of 0.1-mm nichrome wire laid in a thread cut on the outer surface of the block. The wire is insulated from the block by means of Bakelite, as in the case of the controlling thermometer. The resistance of the heater is 2100 ohms.

This arrangement is not inferior in sensitivity to the usual arrangements employed for this purpose, i.e. arrangements incorporating a mirror, a galvanometer, a photocell, and a thyratron relay, and it is superior to them in reliability and convenience. A change in the resistance of the controlling thermometer by 0.01 ohm, i.e. 0.013%, brings about a change in the current in the cryostat heater of 2 ma when the average working current is 10-20 ma. The temperature of the cryostat can be maintained within ± 0.005° for several hours. By way of example, in our work with methanol at pressures in the region of 1 mm, the pressure in the balance case was maintained constant within ± 0.04%.

In order to verify the method, some special experiments were carried out: 1) The working of the cryostat was checked, for which purpose we investigated the dependence of the saturated vapor pressure of heptane on temperature. The experimental results were in close accord with data from the literature. 2) Two series of measurements on well-studied systems were carried out.

1. The adsorption isotherm for methanol vapor was determined at 25° on barium sulfate having a specific surface of 7 sq.m/g (Fig. 4). All of the curves represent the same isotherm, but the scale is subjected to successive

multiplications by 10 with respect to the relative pressure axis. The circles represent our experimental values, and continuous curves are drawn through them. The black spots represent the experimental values obtained by Bering and Serpinsky [1] by the method of independent weighing.

2. The adsorption isotherm for heptane vapor was determined at 20° on homogeneous finely porous silica gel having a specific surface of about 420 sq.m/g (Fig. 5). The signs used are the same as in the preceding graph. The black spots represent the experimental values of Kiselev and coworkers [10], who used an apparatus based on the usual spring sorption balance. It will be seen from these two graphs that the isotherms that we obtained agree quite satisfactorily with those obtained for the same substances by other workers using other methods. It should be noted that in the investigation of adsorption on silica gel, the amount taken was only 12 mg, since with larger amounts the extent of adsorption would have been outside the working range of the balance.

Thus, these verifying experiments showed that the method is suitable for the investigation of the adsorption of vapors on nonporous crystalline adsorbents. Our first systematic measurements of adsorption with this apparatus will form the subject of our second communication.

SUMMARY

1. A precision adsorption apparatus was constructed for the investigation of the adsorption of vapors on nonporous solid adsorbents. It consists of a balance having a sensitivity of $5.7 \cdot 10^{-8}$ g at a load of 1 g and a cryostat for temperatures from −150° to + 50° in which the temperature can be maintained constant within ± 0.005. In this apparatus the effect of mercury vapors and vacuum grease on the adsorbent is excluded, and this increases the reliability of the results and, at the same time, increases the choice of vapors for investigation.

2. Experiments designed to verify the method were carried out, and these showed that it is suitable for accurate adsorption measurements on model adsorbents having specific surfaces of the order of 1 sq.m/g.

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EFFECT OF THE TEMPERATURE FACTOR ON THE RATE OF CORROSION OF METALS IN ELECTROLYTES

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In the theory of corrosion of metals, the hypothesis of the limiting (controlling) factor has received wide application [1, 2]. However, the effect of the limiting factor on the rate of corrosion at high temperatures has not been adequately studied. With the object of determining the effect of temperature on the rate of the corrosion process, we studied the dependence of the current of an iron-zinc couple with varying external resistance on the temperatures of the electrolytes in the cathode and anode spaces. This enabled us to study the part played by the temperature factor for various kinds of control.

EXPERIMENTAL

The results of the experiments showed that the corrosion current increases appreciably with temperature only when the rise in temperature occurs in the space surrounding the electrode associated with the reaction that determines the overall rate. This is illustrated by Fig. 1, from which it follows that, for an iron-zinc couple ($F_a : F_k = 500 : 1$) working with cathodic-ohmic limitation, elevation of the temperature of the electrolyte in the anode space does not result in increased current (see Curve 1).

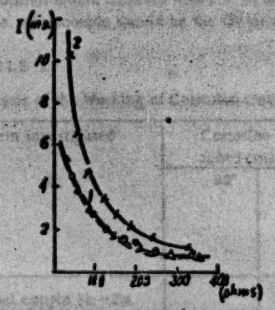

Fig. 1. Dependence of the current of an iron-zinc couple ($F_a : F_k = 1 : 500$) on resistance in 1.0 N NaCl + 0,1N HCl; o- cathode temperature 20°, anode temperature 20°; Δ cathode temperature 20°, anode temperature 80° · x - cathode temperature 80°, anode temperature 20°.

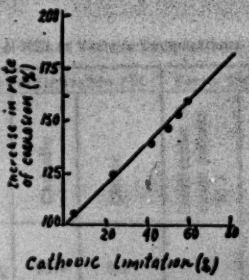

Fig. 2. Dependence of the relative increase of the corrosion current of an iron-zinc couple with rise in temperature on the percentage cathodic limitation.

By changing the external resistance we succeeded in varying the degree of cathodic control from 0 to 60% and were thus able to study the relative change in the corrosion current with increase in degree of cathodic control (Fig. 2). It follows from Fig. 2 that there is a linear relationship between the relative increase in corrosion current and the percentage cathodic limitation. Hence, the more the system is cathodically polarized, the greater will be the effect of change of temperature on the increase in corrosion current. This conclusion is confirmed by a study of the working of a copper-magnesium couple in various electrolytes (Fig. 3). The greatest increase of corrosion with temperature is observed in a 1.5% solution of sodium chloride, i.e. in an electrolyte for which the extent of cathodic control is great for the given couple.

* Deceased

Analysis of the working of the corrosion couples iron - zinc ($F_k : F_a = 1 : 100$) and magnesium - copper ($F_a : F_k = 1 : 100$) having electrodes arranged in one plane, and also of a real microcouple (alloy of zinc with 0.92% of iron), confirmed the laws considered above (Table 1). - The corrosion process of an iron-zinc couple proceeds with cathodic control, and in this system the rate of corrosion increases mainly as a result of increase in the rate of the cathode process. In the corrosion of the magnesium-copper couple anodic and cathodic control are comparable in extent, and with rise in temperature corrosion increases as a result of rise in the rates of both cathodic and anodic processes. The rate of the corrosion process in a real microcouple is determined by the kinetics of the cathode reaction, and with rise of temperature, therefore, corrosion increases as a result of the facilitation of this reaction.

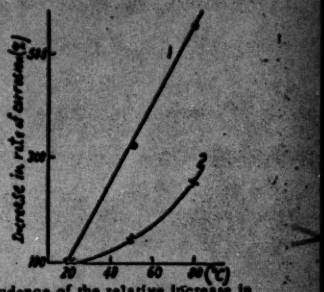

Fig. 3. Dependence of the relative increase in the corrosion current of a magnesium-copper temperature: 1) in 1.5% NaCl; 2) in distilled water.

In the corrosion of metals as the result of the working of a microcouple [2,3,4] the relative amount of ohmic control is negligible and the increase in the conductance of the solution with rise in temperature has no effect on the rate of corrosion; analysis of the working of the microcouple $Zn/FeZn_7$ leads to the same conclusion. In the general case, the variation of the rate of corrosion with rise of temperature is influenced mostly by the variation with temperature of the factor controlling the corrosion process. In macrosystems it is essential to keep to the following rule: so that corrosion in systems in which macrocouples are formed should increase with rise in temperature as little as possible, it is essential that the controlling factor in the macrocouple should be the factor whose resistance would fall with temperature to the least extent.

TABLE 1

Analysis of the Working of Corrosion Couples in 1.0 N NaCl + 0.1 N HCl at Various Temperatures

System investigated	Corrosion current I (ma)		$I_{80°} : I_{20°}$	Extent of limitation (%)			Factor increasing corrosion		
	20°	80°		Anodic	Cathodic	Ohmic	Facilitation of anode process (%)	Facilitation of cathode process (%)	Increase in conductance of solution (%)
Model couple Fe—Zn ($F_a : F_k = 100 : 1$)	0.52	1.7	3.3	3.2	91.3	5.5	7.3	9.2	0.7
Model couple Mg—Cu ($F_k : F_a = 100 : 1$)	12.0	29.0	2.4	47.7	46.0	6.3	55.5	34.0	10.5
Microcouple $Zn/FeZn_7$	3.0	12.0	4	10.7	88.3	1.0	2.55	97.45	0

In actual cases of corrosion the rate of the cathode process may be limited by the rate of ionization of oxygen or the rate of discharge of hydrogen ions. In unstirred electrolytes processes of oxygen depolrization may be controlled also by the rate of the diffusion of oxygen. It was therefore considered to be of interest to study how the rate of corrosion changes with temperature for various forms of cathode process. With this in view we studied the working of the corrosion couples copper-iron, copper-zinc, and copper-magnesium in 1.0 N NaCl + 0.123 N H_2O_2. The electrode areas were 0.2 sq. cm, and the temperature was varied from 0° to 20°. From the corrosion diagrams (Fig. 4) it follows, in the first place, that in all of the couples studied the limiting factor is the rate of the cathode process and, in the second place, that the current of the copper-magnesium couple is determined by the rate of discharge of hydrogen ions, the current of the copper-zinc couple by the rate of diffusion of hydrogen peroxide, and the current of the copper-iron couple by the rate of ionization of oxygen. The temperature coefficients for the rates of corrosion of the couples investigated are given in Table 2.

Analysis of the working of the corrosion couples iron + zinc ($F_k : F_a = 1 : 100$) and magnesium - copper ($F_a : F_k = 1 : 100$) having electrodes arranged in one plane, and also of a real microcouple (alloy of zinc with 0.92% of iron), confirmed the laws considered above (Table 1). The corrosion process of an iron-zinc couple proceeds with cathodic control, and in this system the rate of corrosion increases mainly as a result of increase in the rate of the cathode process. In the corrosion of the magnesium-copper couple anodic and cathodic control are comparable in extent, and with rise in temperature corrosion increases as a result of rise in the rates of both cathodic and anodic processes. The rate of the corrosion process in a real microcouple is determined by the kinetics of the cathode reaction, and with rise of temperature, therefore, corrosion increases as a result of the facilitation of this reaction.

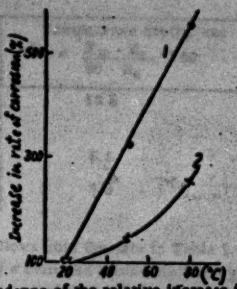

Fig. 3. Dependence of the relative increase in the corrosion current of a magnesium-copper temperature: 1) in 1.5% NaCl; 2) in distilled water.

In the corrosion of metals as the result of the working of a microcouple [2,3,4] the relative amount of ohmic control is negligible and the increase in the conductance of the solution with rise in temperature has no effect on the rate of corrosion. analysis of the working of the microcouple Zn/ $FeZn_7$ leads to the same conclusion. In the general case, the variation of the rate of corrosion with rise of temperature is influenced mostly by the variation with temperature of the factor controlling the corrosion process. In macrosystems it is essential to keep to the following rule: so that corrosion in systems in which macrocouples are formed should increase with rise in temperature as little as possible, it is essential that the controlling factor in the macrocouple should be the factor whose resistance would fall with temperature to the least extent.

TABLE 1

Analysis of the Working of Corrosion Couples in 1.0 N NaCl + 0.1 N HCl at Various Temperatures

System investigated	Corrosion current I (ma)		$I_{80°} : I_{20°}$	Extent of limitation (%)			Factor increasing corrosion		
	20°	80°		Anodic	Cathodic	Ohmic	Facilitation of anode process (%)	Facilitation of cathode process (%)	Increase in conductance of solution (%)
Model couple Fe–Zn ($F_a : F_k = 100 : 1$)	0.52	1.7	3.3	3.2	91.3	5.5	7.3	9.2	0.7
Model couple Mg–Cu ($F_k : F_a = 100 : 1$)	12.0	29.0	2.4	47.7	46.0	6.3	55.5	34.0	10.5
Microcouple Zn/ $FeZn_7$	3.0	12.0	4	10.7	88.3	1.0	2.55	97.45	0

In actual cases of corrosion the rate of the cathode process may be limited by the rate of ionization of oxygen or the rate of discharge of hydrogen ions. In unstirred electrolytes processes of oxygen depolrization may be controlled also by the rate of the diffusion of oxygen. It was therefore considered to be of interest to study how the rate of corrosion changes with temperature for various forms of cathode process. With this in view we studied the working of the corrosion couples copper-iron, copper-zinc, and copper-magnesium in 1.0 N NaCl + 0.125 N H_2O_2. The electrode areas were 0.2 sq. cm, and the temperature was varied from 0° to 20°. From the corrosion diagrams (Fig. 4) it follows, in the first place, that in all of the couples studied the limiting factor is the rate of the cathode process and, in the second place, that the current of the copper-magnesium couple is determined by the rate of discharge of hydrogen ions, the current of the copper-zinc couple by the rate of diffusion of hydrogen peroxide, and the current of the copper-iron couple by the rate of ionization of oxygen. The temperature coefficients for the rates of corrosion of the couples investigated are given in Table 2.

TABLE 2

Temperature Coefficients for the Corrosion Rates of the Couples Copper-Iron, Copper-Zinc, and Copper-Magnesium in 1.0 N NaCl + 0.123 N H_2O_2

Corrosion couple	Limiting Factor	Temperature coefficient $\gamma_k = \frac{K_{30} - K_{10}}{20 \cdot K_{10}} \cdot 100$
Copper-iron	Rate of ionization oxygen	10.6
Copper-zinc	Rate of transport of hydrogen peroxide	3.5
Copper-magnesium	Rate of discharge of hydrogen ions	7.8

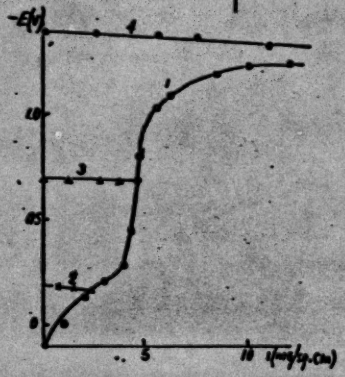

Fig. 4. Polarization curves in 1.0 N NaCl + 0.123 N H_2O_2. 1) cathodic polarization of copper; 2) anodic polarization of iron; 3) anodic polarization of zinc; 4) anodic polarization of magnesium.

It follows from the data in Table 2 that the rate of a corrosion process limited by the rate of transport of the oxidizing agent does not rise with rise in temperature so rapidly as the rates of corrosion processes limited by the rate of the reduction of the oxidizing agent and the rate of discharge of hydrogen ions. The higest temperature coefficient is found when the cathode process is determined by the rate of ionization of oxygen.

SUMMARY

1. The effect of temperature on the rate of corrosion processes having different kinds of limitation was studied for model corrosion couples and for a real microcouple—an alloy of zinc with 0.92% of iron.

2. It was shown that the variation of the rate of the corrosion process with change of temperature is determined primarily by the variation of the factor controlling the corrosion process.

3. The effect of temperature on the rate of corrosion was studied for different kinds of cathodic control: the rate of discharge of hydrogen ions, the rate of diffusion of oxidizing agent (hydrogen peroxide), and the rate of ionization of oxygen. It was shown that the rate of a corrosion process that is limited by the rate of ionization of oxygen shows the greatest increase with rise in temperature, and the rate of the process limited by the rate of transport of the oxidizing agent shows the least increase.

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[3] K. N. Anisimov, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1958 No. 6, 1003 (T.P. 918)*.

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* T. p. = C. B. Translation pagination.

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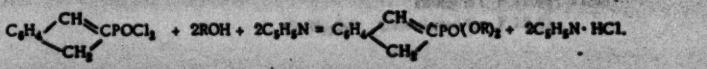
DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 13. DIESTER OF 2-INDENYLPHOSPHONIC ACID

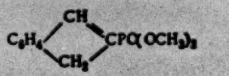
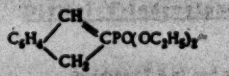
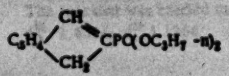
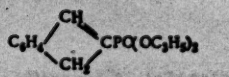
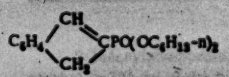
K. N. Anisimov and A. N. Nesmeyanov

Diesters of 2-indenylphosphonic acid were prepared by the method used for the synthesis of 2-aryl and 2-alkoxy-vinylphosphonic esters, namely, by the action of 2-indenylphosphonic dichloride on alcohols in presence of pyridine in a benzene or petroleum ether medium [1-3]:

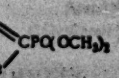


2-Indenylphosphonic esters are clear liquids of high boiling point. They are all soluble in organic solvents. Below, we give a table of constants for the esters obtained.

TABLE

Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
	146 (2)	1.5603	1.2109
	150 (1)	1.5398	1.1410
	162 (1)	1.5298	1.1392
	169 (1)	1.5514	.1354
	206 (2)	1.5100	1.0220

EXPERIMENTAL

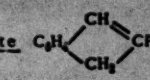
Dimethyl 2-Indenylphosphonate 

A solution of 11.65 g of 2-indenylphosphonic dichloride in 20 ml of benzene was added to a stirred mixture of 150 g of dry benzene, 7.9 g of pyridine, and 3.2 g (4 ml was taken) of absolute methanol. When reaction was complete, pyridine hydrochloride was separated and the filtrate was washed with 3% sodium carbonate solution and dried over sodium sulfate. Excess of alcohol and benzene was distilled off, and vacuum fractionation of the residue yielded 8.5 g (50.3%) of a substance having b.p. 146° (2 mm); n_D^{20} 1.5603, d_4^{20} 1.2109.

Found %: P 13.70; 13.78

$C_{11}H_{17}O_3P$. Calculated %: P 13.83

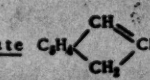
All of the other esters of 2-indenylphosphonic acid were prepared by this method.

Diethyl 2-Indenylphosphonate 

2-Indenylphosphonic dichloride (12 g) was added to 8.2 g of pyridine and 5 g of absolute ethanol. Vacuum fractionation gave 7.8 g (60%) of a substance having b.p. 150° (1mm); n_D^{20} 1.5298; d_4^{20} 1.1410.

Found %: P 11.89; 11.99

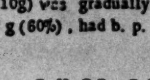
$C_{13}H_{17}O_3P$ Calculated %: P 12.31

Dipropyl 2-Indenylphosphonate 

2-Indenylphosphonic dichloride (10g) was gradually added to 15.1 g of absolute propyl alcohol and 6.8 g of pyridine. The product, amounting to 7 g (60%), had b. p. 162° (1mm); n_D^{20} 1.5298; d_4^{20} 1.1392.

Found %: P 10.49; 10.40

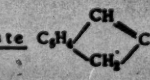
$C_{15}H_{21}O_3P$. Calculated %: P 10.71

Diallyl 2-Indenylphosphonate 

Pyridine (7.9 g) and absolute allyl alcohol (5.8 g) were added to 11.65 g of 2-indenylphosphonic dichloride. The reaction was carried out in a benzene medium. The product, amounting to 8.2 g (61 %), had b.p.169° (1mm); n_D^{20} 1.5514; d_4^{20} 1.1354.

Found %: P 11.05; 11.17

$C_{15}H_{17}O_3P$. Calculated %: P 11.23

Dihexyl 2-Indenylphosphonate 

2-Indenylphosphonic dichloride (13 g) was added to a stirred solution of 8.8 g of pyridine and 11.3 g of hexyl alcohol in 170 ml of dry benzene. The product, amounting to 12.8 g (63%), had b.p. 206° (2mm); n_D^{20} 1.5100; d_4^{20} 1.0220

Found %: P 8.55; 8.47

$C_{21}H_{33}O_3P$. Calculated %: P 8.51

SUMMARY

Five esters of 2-indenylphosphonic acid were prepared and characterized.

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* T. p. = C. B. Translation pagination.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 17. DERIVATIVES OF STYRYLPHOSPHONIC ACID

K. N. Anisimov and A. N. Nesmeyanov

N,N,N,N-Tetraalkyl-P-styrylphosphonic Diamides. N,N,N,N-Tetraalkyl derivatives of P-styrylphosphonic diamide were prepared in the same way as the tetraalkyl derivatives of P-2-alkoxyvinylphosphonic diamide, i.e. by reaction of one molecular equivalent of styrylphosphonic dichloride with four molecular equivalents of a dialkylamine in a petroleum ether or benzene medium [1]:

$$C_6H_5-CH=CHPOCl_2 + 4R_2NH = C_6H_5-CH=CHPO[N(R_2)]_2 + 2R_2NH\cdot HCl.$$

In this way we synthesized tetramethyl, tetraethyl, tetrapropyl, tetrabutyl, and bispentamethylene derivatives of P-styrylphosphonic diamide. The tetramethyl and tetrapropyl derivatives are viscous liquids having high boiling points and refractive indices; the other compounds are crystalline substances, soluble in the usual organic solvents, but not in water.

The N,N,N,N,- tetraalkyl - P - styrylphosphonic diamides obtained are listed in Table 1.

TABLE 1

Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5-CH=CHPO[N(CH_3)_2]_2$	180 (2)	1.5665	1.0818
$C_6H_5-CH=CHPO[N(C_2H_5)_2]_2$	103.5*		
$C_6H_5-CH=CHPO[N(C_3H_7\text{-}n)_2]_2$	192 (2)	1.5290	1.0060
$C_6H_5-CH=CHPO[N(C_4H_9\text{-}n)_2]_2$	39 - 40*		
$C_6H_5-CH=CHPO[NC_5H_{10}]_2$	135 - 136*		

* Melting point

O,O-Dialkyl Styrylphosphonothioates. We prepared O,O-dimethyl and O,O-diethyl styrylphosphonothioates by reaction of styrylphosphonothioic dichloride with sodium alkoxides in methanol and ethanol, respectively:

$$C_6H_5-CH=CHPSCl_2 + 2NaOR = C_6H_5CH=CHPS(OR)_2 + 2NaCl.$$

The O,O-dialkyl styrylphosphonothioates obtained are clear liquids, insoluble in water, but soluble in many organic solvents. The constants of these compounds are given in Table 2.

TABLE 2

Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5-CH=CHPS(OCH_3)_2$	124 (1)	1.5890	1.1794
$C_6H_5-CH=CHPS(OC_2H_5)_2$	130 (1)	1.5658	1.1067

S,S-Dialkyl and Diaryl Styrylphosphonodithioates. We obtained two compounds of this series — S,S-diethyl and S, S-diphenyl styrylphosphonodithioates. The first of these was synthesized by the action of styrylphosphonic dichloride on sodium ethyl mercaptide in an ether medium. The diethyl ester is a viscous liquid of unpleasant odor,

soluble in the usual organic solvents. The second ester was prepared by the action of styrylphosphonic dichloride on benzenethiol in presence of pyridine in a benzene medium. It is a crystalline substance, insoluble in water, but soluble in organic solvents. Data relating to these compounds are given in Table 3.

TABLE 3

Formula of compound	B.p. in °C(p in mm)	n_D^{20}	d_4^{20}
$C_6H_5-CH=CHPO(SC_6H_5)_2$	168(1)	1.6248	1.1469
$C_6H_5-CH=CHPO(SC_6H_5)_2$	117 •		

• Melting point.

EXPERIMENTAL

N,N,N,N-Tetramethyl-P-styrylphosphonic Diamide $C_6H_5CH=CHPO[N(CH_3)_2]_2$. Styrylphosphonic dichloride (11.05 g) was added dropwise to a stirred solution of 9 g of dimethylamine in a cooled mixture of 70 ml of petroleum ether and 30 ml of benzene. When the whole of the acid chloride had been added, stirring was continued for two hours. On the next day the reaction mixture was heated in a water bath for two hours at 30-35°. The precipitate was filtered off and washed twice with petroleum ether. The filtrate was treated with small portions of saturated caustic soda solution to remove traces of dimethylamine hydrochloride, dried over calcined potassium carbonate, and fractionated. The product isolated, amounting to 6 g(50.8%), had b.p. 180° (2 mm); n_D^{15} 1.5665, d_4^{20} 1.0818.

Found %: N 11.39; 11.56

$C_{10}H_{15}OPN_2$. Calculated %: N 11.78

N,N,N,N-Tetraethyl-P-styrylphosphonic Diamide $C_6H_5CH=CHPO[N(C_2H_5)_2]_2$ Styrylphosphonic dichloride (11.05 g) was added gradually to a solution of 14.5 g of diethylamine in 150 ml of a mixture of petroleum ether and benzene. The product, amounting to 8 g(78.4%), melted at 103.5°.

Found %: N 9.10; 9.10

$C_{18}H_{27}OPN_2$. Calculated %: N 9.52

N,N,N,N-Tetrapropyl-P-styrylphosphonic Diamide $C_6H_5CH=CHPO[N(C_3H_7-n)_2]_2$. Reaction of 20.2 g of dipropylamine and 11.05 g of styrylphosphonic dichloride gave 13 g of tetrapropyl-P-styrylphosphonic diamide, b.p. 192° (2 mm); n_D^{20} 1.5290; d_4^{20} 1.0050.

Found %: P 8.76; 8.97

$C_{22}H_{39}PON_2$ Calculated %: P 8.83

N,N,N,N-Tetrabutyl-P-styrylphosphonic Diamide $C_6H_5CH=CHPO[N(C_4H_9-n)_2]_2$. Styrylphosphonic diamide (11 g) was added to a solution of 27 g of dibutylamine in 150 ml of petroleum ether. The usual treatment yielded 8 g of tetrabutyl-P-styrylphosphonic diamide, m.p. 39-40°.

Found %: P 7.59; 7.77

$C_{26}H_{47}PON_2$. Calculated %: P 7.63

N,N-Dispentamethylene-P-styrylphosphonic Diamide (Styrylphosphonic Dipiperidide) $C_6H_5CH=CHPO\cdot[N-C_5H_{10}]_2$. Styrylphosphonic dichloride (11 g) was added to a cooled(ice water) stirred solution of 16 g of piperidine in 125 ml of petroleum ether. The product was a crystalline substance which melted at 135-136° after being recrystallized from ether.

Found %: N 8.74; 8.65

$C_{18}H_{27}PON_2$ Calculated %: N 8.80

O,O-Dimethyl Styrylphosphonothioate $C_6H_5CH=CHPS(OCH_3)_2$. Styrylphosphonothioic dichloride (11.85 g) was added with cooling and stirring to sodium methoxide prepared from 2.3 g of sodium and 60 ml of absolute methanol. When reaction was complete the mixture was diluted with 120 ml of absolute ether. The product isolated, amounting to 8.3 g (65.3%), had b. p. 124° (1 mm); n_D^{20} 1.5890; d_4^{20} 1.1704.

Found %: P 13.47; 13.36

$C_{10}H_{13}O_2PS$. Calculated %: P 13.59

O,O-Diethyl Styrylphosphonothioate $C_6H_5CH=CPS(OC_2H_5)_2$. Styrylphosphonothioic dichloride (11.85 g) was added to a stirred solution of sodium ethoxide, prepared from 2.3 g of sodium and 70 ml of absolute ethanol. The product isolated, amounting to 7.6 g (55.4%), had b. p. 130° (1 mm); n_D^{20} 1.5658; d_4^{20} 1.1067.

Found %: P 12.00; 12.17

$C_{12}H_{17}O_2PS$. Calculated %: P 12.10

S,S-Diethyl Styrylphosphonodithioate $C_6H_5CH=CHPO(SC_2H_5)_2$. Styrylphosphonic dichloride (11.05 g) was added to a cooled stirred solution of sodium ethyl mercaptide, prepared in absolute ether from 2.3 g of sodium and 9 g of ethanethiol. The product isolated, amounting to 8 g (58.8%), had b. p. 168° (1 mm); n_D^{20} 1.6248; d_4^{20} 1.1469.

Found %: P 11.31; 11.39

$C_{12}H_{17}OPS_2$. Calculated %: P 11.39

S,S-Diphenyl Styrylphosphonodithioate $C_6H_5CH=CHPO(SC_6H_5)_2$. Styrylphosphonic dichloride (11.05 g) was added to a cooled stirred solution of 11 g of benzenethiol and 7.9 g of pyridine in 150 ml of dry benzene. The product isolated (9.8 g) was S,S-diphenyl styrylphosphonodithioate, m.p. 117°.

Found %: C 65.68; 65.67; H 4.93; 4.74; S 17.23; 17.59

$C_{20}H_{17}OPS_2$. Calculated %: C 65.48; H 4.61; S 17.39

SUMMARY

Five N-substituted P-styrylphosphonic diamides, two O,O-diesters of styrylphosphonothioic acid, and two S,S-diesters of styrylphosphonodithioic acid were synthesized and characterized.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 18. 2-(ALKYLTHIO)VINYLPHOSPHONIC DICHLORIDES AND THEIR DERIVATIVES

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

Derivatives of unsaturated phosphonic acids, a class of compounds that has received very little study, are of great interest. Continuing our study of the addition of PCl_5 to vinyl ethers, we decided to investigate examples in which vinyl thioethers were used. These thioethers have become accessible as a result of a simple and convenient method of synthesis developed by Shostakovsky and his students [1].

We consider that PCl_5 adds to vinyl thioethers in the same way as it adds to vinyl ethers, i.e. in accord with Markovnikov's rule:

$$RS-CH=CH_2 + 2PCl_5 = RSCHCl-CH_2PCl_4 \cdot PCl_5$$
$$RSCHCl-CH_2PCl_4 \cdot PCl_5 + 2SO_2 = RSCH=CHPOCl_2 + 2SOCl_2 + POCl_3 + HCl.$$

By this reaction we prepared 2-(ethylthio)- and 2-(butylthio)-vinylphosphonic dichlorides in 68-80% yield. Constants of these compounds are given in Table 1.

TABLE 1

Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_2H_5-S-CH=CHPOCl_2$	117(2)	1.5720	1.3938
$n-C_4H_9-S-CH=CHPOCl_2$	120-122(1)	1.5505	1.2845

2-(Alkylthio)vinylphosphonic dichlorides are liquids of unpleasant odor which rapidly decolorize bromine water and which react with alcohols and dialkylamines. They are soluble in many organic solvents.

2-(Alkylthio)vinylphosphonic Esters. In order to make a more detailed study of the properties of 2-(alkylthio)vinylphosphonic dichlorides, we undertook the synthesis of diesters by the method of Milobendzki and Sachnowski [2].

$$RS-CH=CHPOCl_2 + 2ROH + 2C_5H_5N = RS-CH=CHPO(OR)_2 + 2C_5H_5N \cdot HCl.$$

By this method we obtained the dipropyl, dibutyl, diallyl, and dihexyl esters of 2-(ethylthio) and 2-(butylthio)-vinylphosphonic acids in 75-83% yield. Constants of these compounds are given in Table 2.

Diesters of 2-alkylthio)vinylphosphonic acids are clear liquids, which are readily distilled under reduced pressure, rapidly decolorize bromine water, and are of good solubility in organic solvents, but insoluble in water.

N,N,N,N-Tetraalkyl-P-2-(alkylthio)vinylphosphonic Diamides. We prepared tetraalkyl-P-2(alkylthio) vinylphosphonic diamides by the method of Michaelis [3].

$$RS-CH=CHPOCl_2 + 4R_2NH = RS-CH=CHPO[N(R)_2]_2 + 2R_2NH \cdot HCl.$$

By this reaction we obtained 2-(ethylthio)vinylphosphonic dipiperidide in 80-82% yield ($C_2H_5-S-CH=CHPO[NC_5H_{10}]_2$, m. p. 62.5°.

EXPERIMENTAL

2-(Ethylthio)vinylphosphonic Dichloride $C_2H_5SCH=CHPOCl_2$. To a stirred cooled (ice water) benzene suspension of 83 g of PCl_5, 17.6 g of ethyl vinyl sulfide (b.p. 91.9-92.5°, n_D^{20} 1.4756) was added dropwise. When addition of ethyl vinyl sulfide was complete, the reaction mixture became very hot, and there was a copious evolution of hydrogen chloride. The resulting crystalline complex was left overnight. On the next day the reaction mixture was subjected to the action of sulfur dioxide, which was passed until the crystalline mass dissolved completely. After removal of solvent phosphoryl chloride, and thionyl chloride by distillation, the residue was vacuum-fractionated and yielded 28 g (68 %) of a substance having b.p. 117° (2 mm); n_D^{20} 1.5720; d_4^{20} 1.3936

Found %: P 14.87; 14.91
$C_4H_7PSOCl_2$. Calculated %: P 15.12

2-(Butylthio)vinylphosphonic Dichloride $n-C_4H_9SCH=CHPOCl_2$. 2-(Butylthio)vinylphosphonic dichloride was prepared under the conditions described above, 27 g of butyl vinyl sulfide being added gradually to 85 g of PCl_5. The product, amounting to 37 g (82 %), had b.p. 120-122° (1 mm); n_D^{20} 1.5505; d_4^{20} 1.2845

Found %: P 13.46; 13.53
$C_6H_{11}PSOCl_2$. Calculated %: P 13.30

Dipropyl 2-(Ethylthio)vinylphosphonate $C_2H_5SCH=CHPO(OC_3H_7-n)_2$. 2-(Ethylthio)vinylphosphonic dichloride (10.3 g) was added to a stirred mixture of 100 ml of benzene, 6.2 g of propyl alcohol, and 8.5 g of pyridine. The product, amounting to 8 g, had b.p. 147° (2 mm); n_D^{20} 1.4930; d_4^{20} 1.0807

Found %: C 47.28; 47.20; H 8.39; 8.33
$C_{10}H_{21}PSO_3$. Calculated %: C 47.61; H 8.33

Dibutyl 2-(Ethylthio)vinylphosphonate $C_2H_5SCH=CHPO(OC_4H_9-n)_2$. 2-(Ethylthio)vinylphosphonic dichloride (10 g) was added to a stirred mixture of 7.6 g of butyl alcohol, 8.3 g of pyridine, and 150 ml of dry benzene. The product (9.5 g), obtained by vacuum fractionation, had b.p. 168° (3mm); n_D^{20} 1.4890; d_4^{20} 1.0317

Found %: C 50.98; 51.11; H 9.01; 8.96
$C_{12}H_{25}PSO_3$. Calculated %: C 51.42; H 8.92

Diallyl 2-(Ethylthio)vinylphosphonate $C_2H_5SCH=CHPO(OC_3H_5)_2$. 2-(Ethylthio)vinylphosphonic dichloride (10.2 g) was caused to react with 5.8 g of allyl alcohol in presence of 8g of pyridine. Vacuum fractionation yielded 8.3 g of a substance having b.p. 134° (1 mm); n_D^{20} 1.5120; d_4^{20} 1.1119

Found %: P 11.98; 12.11
$C_{10}H_{17}PSO_3$. Calculated %: P 12.50

Dihexyl 2-(Ethylthio)vinylphosphonate $C_2H_5SCH=CHPO(OC_6H_{13}-n)_2$. This substance (14.5 g) was obtained by reaction of 10.2 g of 2 (ethylthio)vinylphosphonic dichloride with 10.5 g of hexyl alcohol in presence of 8.2 g of pyridine. It had b.p. 165° (1 mm); n_D^{20} 1.4808; d_4^{20} 1.0059

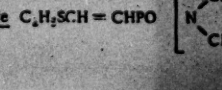
Found %: P 9.39; 9.22
$C_{18}H_{39}PSO_3$. Calculated %: P 9.50

Bis(2-methoxyethyl) 2-(Ethylthio)vinylphosphonate $C_2H_5SCH=CHPO(OCH_2CH_2OCH_3)_2$. When treated with 7.6 g of 2-methoxyethanol and 8 g of pyridine, 10.5 g of 2-(ethylthio)vinylphosphonic dichloride gave 9.2 g of a substance having b.p. 160-161° (1 mm); n_D^{20} 1.4925; d_4^{20} 1.1512

Found %: P 10.66; 10.79
$C_{10}H_{21}PO_5S$. Calculated %: P 10.91

Bis(2-ethoxyethyl) 2-(Ethylthio)vinylphosphonate $C_2H_5SCH=CHPO(OCH_2CH_2OC_2H_5)_2$. Reaction between 10.2 g of 2-(ethylthio)vinylphosphonic dichloride, 9 g of 2-ethoxyethanol, and 8 g of pyridine gave 12.5 g of a substance having b.p.168° (1 mm); n_D^{20} 1.4865; d_4^{20} 1.1056

Found %: P 9.91; 9.87
$C_{12}H_{25}PO_5S$. Calculated %: P 9.33

2-(Ethylthio)vinylphosphonic Dipiperidide $C_2H_5SCH=CHPO$ 

Reaction of 15 g of 2-(ethylthio)vinylphosphonic dichloride with 25 g of piperdine in a mixture of petroleum ether and diethyl ether gave 16 g of the dipiperidide, m. p. 62.5°.

Found %: P 10.72; 10.66

$C_{14}H_{27}PON_2S$. Calculated %: P 10.26

Dibutyl 2-(Butylthio)vinylphosphonate n-$C_4H_9SCH=CHPO(OC_4H_9\text{-}n)_2$. Reaction between 11.65 g of 2-(butylthio)vinylphosphonic dichloride, 6.5 g of butyl alcohol, and 8 g of pyridine gave 11 g of ester, b.p.153-154° (2 mm); n_D^{20} 1.4848; d_4^{20} 1.0235.

Found %: C 54.06; 54.15; H 9.27; 9.30

$C_{14}H_{29}PSO_3$. Calculated %: C 54.54; H 9.41

Diallyl 2-(Butylthio)vinylphosphonate n-$C_4H_9SCH=CHPO(OC_3H_5)_2$. This ester (9 g) was obtained by reaction between 6 g of allyl alcohol and 11.7 g of 2-(butylthio)vinylphosphonic dichloride in presence of 8.3 g of pyridine in a benzene medium. It had b.p.146° (1 mm); n_D^{20} 1.5049; d_4^{20} 1.0800.

Found %: P 11.23; 11.13

$C_{12}H_{21}PO_3S$. Calculated %: P 11.29

Dihexyl 2-(Butylthio)vinylphosphonate n-$C_4H_9SCH=CHPO(OC_6H_{13}\text{-}n)_2$. 2-(Buthylthio)vinylphosphonic dichloride (11.65 g) was added to a stirred mixture of 10.2 g of hexyl alcohol and 8 g of pyridine. The resulting ester (12.5 g) had b.p.201° (2 mm); n_D^{20} 1.4790; d_4^{20} 1.0009.

Found %: P 8.48; 8.53

$C_{18}H_{37}PO_3S$. Calculated %: P 8.51

SUMMARY

The following compounds were prepared and characterized: 2-(ethylthio)vinylphosphonic and 2-(butylthio)vinylphosphonic dichlorides; dipropyl, dibutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) 2-(ethylthio)vinylphosphonates; dibutyl, diallyl, and dihexyl 2-(butylthio)vinylphosphonates; and 2-(ethylthio)vinylphosphonic dipiperidide.

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REACTIONS OF ORGANOMERCURY BASES WITH UNSATURATED COMPOUNDS •

I. F. Lutsenko and E. I. Yurkova

Organomercury bases and their reactions have received relatively little study. It is known that organomercury hydroxides are readily arylated by aromatic compounds of tin, antimony, and boron with formation of unsymmetrical mercury compounds of the type RHgR' [1] and that they have found application as mercurating agents, being among the most powerful known [2]. In recent years, Razuvaev and coworkers have made extensive investigations into the mechanism of the photochemical decomposition of arylmercury hydroxides and the behavior of the resulting radicals in solvents having various dielectric constants [3]. Arylmercury hydroxides, however, can react not only by the radical mechanism, but also by an ionic mechanism, which is associated with the dissociation:

$$RHgOH \rightleftharpoons RHg^{+} + OH^{-}.$$

It is probable that organomercury bases react in this form also in the recently discovered reaction between moist mercuric oxide and a vinyl ether [4], which gives compounds in which a mercury atom is substituted into two molecules of a carbonyl compound:

$$HgO + H_2O + CH_2 = CHOR \longrightarrow \left[HOHgCH_2CH\begin{matrix}OR\\OH\end{matrix}\right] \xrightarrow{CH_2 = CHOR} Hg(CH_2CHO)_2.$$

The intermediately formed (hydroxymercury) acetaldehyde adds to a further molecule of the vinyl ether and yields the full organomercury compound. If the scheme proposed for the course of the reaction is correct then it may be expected that other organomercury bases will add at carbon-carbon double bonds.

We therefore investigated the behavior of phenyl- and p-tolyl-mercury hydroxides toward some unsaturated hydrocarbons (1-hexene, 1-heptene, cyclohexene, styrene, and 1,1-diphenylethylene), vinyl ethers (ethyl vinyl, isopropyl vinyl, butyl vinyl, and ethyl isopropenyl ethers), and ketene diethyl acetal.

Attempts to bring about the addition of arylmercury hydroxides to α-olefins in accordance with the scheme

$$ArHgOH + RCH = CH_2 \xrightarrow{CH_3OH} \begin{matrix}RCH - CH_2HgAr\\|\\OCH_3\end{matrix}$$

were not successful; treatments were carried out both in the cold, and also at the boil (45 minutes in a water bath), in all of the experiments, the arylmercury hydroxide was recovered in yields of more than 90%.

Hence, in these α-olefins of various structure the double bond was found to be inert toward arylmercury hydroxides. On the other hand, vinyl ethers, in which the double bond is more active, react readily even in the cold with a methanol solution of an arylmercury hydroxide. On the basis of the considerations given in the previous paper [4], it may be expected that this reaction will result in the formation of a full unsymmetrical organomercury compound in accordance with the following equation:

$$ArHgOH + CH_2 = CHOR \xrightarrow{CH_3OH} ArHgCH_2CH\begin{matrix}OR\\OCH_3\end{matrix}$$

In all of the experiments on the various vinyl ethers we were unable to isolate the mixed acetal of the (arylmercuri)acetaldehyde, a result that is probably to be associated with the extreme lability of compounds of this type.

• Communication from A. N. Nesmeyanov's laboratory

It is well known that full organomercury compounds of the type RHgR' are unstable, undergoing decomposition even at ordinary temperature into a mixture of the two symmetrical compounds R_2Hg and R'_2Hg. For the mixed acetal of an (arylmercuri) acetaldehyde this process must occur particularly readily as the result of the presence of a labile C—Hg bond, which is ruptured already by 0.25 N HCl. As a result of the disproportionation, the mixed acetal of the (arylmercuri) acetaldehyde should yield two compounds — a diarylmercury and a mixed acetal of mercuridiacetaldehyde:

$$2ArHgCH_2CH\begin{matrix}OR\\OCH_3\end{matrix} \longrightarrow Ar_2Hg + Hg\left(CH_2CH\begin{matrix}OR\\OCH_3\end{matrix}\right)_2.$$

It was in fact found that in all of the investigated reactions between arylmercury hydroxides and vinyl ethers the diarylmercury was obtained in almost quantitative yield. Considerable difficulties were encountered in the isolation of the second reaction product — the mixed acetal of mercuridiacetaldehyde — since it is a heavy oil, readily decomposed by heat so that it cannot be purified by distillation. It must be pointed out that diarylmercury is appreciably soluble in this oil, which made it still more difficult to isolate the second reaction product and prove its structure. As all attempts to isolate the mixed acetal of mercuridiacetaldehyde in an analytically pure form failed, the formation of this compound was proved by the following two reactions. The oil remaining after separation of the bulk of the diarylmercury was dissolved in alcohol and the solution was mixed with an alcoholic solution of mercuric chloride. The (chloromercuri) acetaldehyde that separated was characterized by analysis and by a mixture melting test with an authentic sample. The separation of (chloromercuri)acetaldehyde instead of its mixed acetal is to be attributed to the hydrolysis of the latter by hydrogen chloride formed in the alcoholysis of the mercuric chloride. The reaction can be represented as follows:

$$Hg\left(CH_2CH\begin{matrix}OR\\OCH_3\end{matrix}\right)_2 + HgCl_2 \xrightarrow{CH_3OH-H_2O} 2ClHgCH_2CHO + ROH + CH_3OH.$$

The formation of a mixed acetal of mercuridiacetaldehyde by reaction of an arylmercury hydroxide with a vinyl ether can be proved also by hydrolysis of the acetal and isolation of mercuridiacetaldehyde. It is in fact found that, when an alcoholic solution of the unpurified mixed acetal of mercuridiacetaldehyde (remaining after separation of the diarylmercury) is boiled with traces of hydrochloric acid, the acetal is hydrolyzed and mercuridiacetaldehyde — characterized by analysis and by a mixture melting test with an authentic sample — is obtained in high yield. In an analogous way, reaction between phenylmercury hydroxide and ethyl isopropenyl ether yielded diphenylmercury and mercuridiacetone.

The addition reaction between an arylmercury hydroxide and a vinyl ether can be used preparatively for the symmetrization of organomercury salts under very mild conditions. In this reaction there is no need to isolate the arylmercury hydroxide obtained by boiling an organomercury salt with methanolic caustic potash; this fact is shown by the reactions of phenyl- and p-tolyl-mercury chlorides with vinyl ethers in an alkaline medium. It would appear that this method can be used for the symmetrization of products formed by the addition of mercury salts at a double bond, a process that cannot be effected by the use of the usual symmetrizing agents (both reducing agents and complex-forming agents).

Ketene diethyl acetal, which contains an extremely active double bond, reacts with phenylmercury hydroxide with evolution of an appreciable amount of heat. From the reaction mixture we isolated diphenylmercury in high yield. Hence, by analogy with the reaction of an arylmercury hydroxide with a vinyl ether, considered above, it must be supposed that the intermediately formed ethyl (phenylmercuri) acetate is unstable and decomposes into diphenylmercury and diethyl mercuridiacetate. The whole process can be represented as follows:

$$CH_2=C(OC_2H_5)_2 + C_6H_5HgOH \longrightarrow \left[C_6H_5HgCH_2C\begin{matrix}OC_2H_5\\OC_2H_5\\OH\end{matrix}\right] \longrightarrow$$

$$\xrightarrow{-C_2H_5OH} \left[C_6H_5HgCH_2C\begin{matrix}O\\OC_2H_5\end{matrix}\right] \longrightarrow (C_6H_5)_2Hg + Hg\left(CH_2C\begin{matrix}O\\OC_2H_5\end{matrix}\right)_2.$$

It was not found possible to isolate the diethyl mercuridiacetate from the oily readily decomposed residue remaining after separation of diphenylmercury. However, when an alcohol solution of mercuric chloride was added

to this oily residue, a low yield was obtained of a crystalline compound corresponding in analysis to the expected ethyl (chloromercuri) acetate. It was thus shown that organomercury bases are able to add at the double carbon-carbon bond of a vinyl ether or of ketene diethyl acetal.

EXPERIMENTAL

Reaction of Phenylmercury Hydroxide with Ethyl Vinyl Ether. Ethyl vinyl ether (2 g) was added to a filtered solution of 3 g (0.01 mole) of phenylmercury hydroxide in 140 ml of methanol. On the next day the solution was evaporated down to two-thirds bulk under reduced pressure. The diphenylmercury that separated was filtered off at the pump. The yield was 1.7 g (94%). The substance had m.p. 118-120°, undepressed by admixture of authentic diphenylmercury.

Found%: Hg 56.55; 56.41
$(C_6H_5)_2Hg$. Calculated%: Hg 56.50

Methanol was driven from the filtrate under reduced pressure, and the oil that remained was dissolved in an equal volume of alcohol and added to an alcoholic solution of 1.8 g of mercuric chloride. The mixture was heated for a short time and cooled; the precipitate of phenylmercury chloride was filtered off. It had m.p. 252-253°, undepressed by admixture of an authentic sample.

The remaining solution was completely freed from alcohol under reduced pressure. The crystalline precipitate that formed was found to be (chloromercuri)acetaldehyde, amounting to 0.9 g (75%).. After crystallization from dichloroethane it had m.p. 128-129°, undepressed by admixture of an authentic sample.

Found%: Hg 71.50; 71.75
$ClHgCH_2CHO$. Calculated%: Hg 71.88

Reaction of Phenylmercury Hydroxide with Ethyl Vinyl Ether. Isolation of Mercuridiacetaldehyde. Under similar conditions a solution of 6 g of phenylmercury hydroxide was brought into reaction with 4 g of ethyl vinyl ether. The yield of diphenylmercury was quantitative; it had m.p. 120-122°. The oil remaining after separation of diphenylmercury was dissolved in an equal volume of alcohol, and the solution was acidified with a drop of concentrated hydrochloric acid (as little as possible of the acid must be taken), heated to the boil, filtered, and set aside to crystallize. Crystals of mercuridiacetaldehyde formed, and were separated and washed with absolute ether. The yield was 0.8 g (66%). The substance melted at 92-93° and there was no depression in admixture with mercuridiacetaldehyde prepared from mercuric oxide and ethyl vinyl ether.

Found%: Hg 69.75; 69.91
$Hg(CH_2CHO)_2$. Calculated%: Hg 69.97

Reactions of Phenylmercury Hydroxide with Butyl Vinyl Ether and with Isopropyl Vinyl Ether. Reaction, under the conditions described above, between 3 g (0.01 mole) of phenylmercury hydroxide and 2 g of butyl vinyl ether yielded 1.7 g (94%) of diphenylmercury, m.p. 120°, and 0.9 g (75%) of mercuridiacetaldehyde, m.p. 92-93°.

Found%: Hg 69.73; 69.82
$Hg(CH_2CHO)_2$. Calculated%: Hg 69.97

The same results were obtained when butyl vinyl ether was replaced by isopropyl vinyl ether.

Reactions of p-Tolylmercury Hydroxide with Ethyl Vinyl and Butyl Vinyl Ethers. Ethyl vinyl ether (2 g) was added to a filtered solution of 3.1 g (0.01 mole) of p-tolylmercury hydroxide in 120 ml of methanol. On the next day one-third of the solvent was removed under reduced pressure, and the di-p-tolylmercury that separated was filtered off. The yield was 1.7 g (90%). The substance melted at 237-238°.

Found%: C 43.23; H 3.75; Hg 51.60
$(C_7H_7)_2Hg$. Calculated%: C 43.90; H 3.66; Hg 52.35

Mercuridiacetaldehyde, m.p. 92-93°, was isolated from the filtrate in the way described above. There was no depression in a mixture melting test.

Found%: Hg 69.90
$Hg(CH_2CHO)_2$. Calculated%: Hg 69.97

Similar results were obtained also in the reaction of p-tolylmercury hydroxide with butyl vinyl ether.

Symmetrization of Phenylmercury Chloride. Caustic potash, as a 40% methanolic solution (26.5 ml), was added to a solution of 5 g of phenylmercury chloride in 100 ml of methanol, and the mixture was boiled for 30 minutes. The mixture was cooled and filtered, and 1.5-2 g of ethyl vinyl ether was added to the filtrate. On the next day one-third of the solvent was distilled off, and the diphenylmercury that separated was filtered off. The yield was 2.6 g (92%). It had m.p. 119-120°, undepressed by admixture of authentic diphenylmercury.

Found%: Hg 56.46; 56.41
$(C_6H_5)_2Hg$. Calculated%: Hg 56.50

Symmetrization of p-Tolylmercury Chloride. Reaction, under similar conditions, between 5 g of p-tolylmercury chloride and 2 g of ethyl vinyl ether yielded 2.7 g (95%) of di-p-tolylmercury, m.p. 237-238°.

Found%: Hg 52.23; 52.32
$(C_7H_7)_2Hg$. Calculated%: Hg 52.35

Reaction of Phenylmercury Hydroxide with Ethyl Isopropenyl Ether. Ethyl isopropenyl ether (1 g) was added to a solution of 1 g of phenylmercury hydroxide in 50 ml of methanol. The further treatment was as described above, and a quantitative yield of diphenylmercury, m.p. 118-120°, was obtained.

Found%: Hg 56.44; 56.54
$(C_6H_5)_2Hg$. Calculated%: Hg 56.50

The oil remaining after the separation of diphenylmercury was acidified with a drop of hydrochloric acid, and mercuridiacetone, amounting to 0.25 g (45%), was isolated. It had m.p. 67-68°, undepressed by admixture of an authentic sample.

Found%: Hg 63.70
$Hg(CH_2COCH_3)_2$. Calculated%: Hg 63.74

Reaction of Phenylmercury Hydroxide with Ketene Diethyl Acetal. Phenylmercury hydroxide, amounting to 3 g (0.01 mole), was added gradually to 3 g of ketene diethyl acetal. Reaction set in immediately with evolution of some heat, and the whole of the phenylmercury hydroxide dissolved. On the next day a ten-fold amount of absolute ether was added to bring about the separation of the polymer of ketene diethyl acetal. The polymer was filtered off, and two-thirds of the ether was evaporated off. The diphenylmercury that separated was filtered off and washed with ether. The yield was 1.6 g (88%). It had m.p. 118-120°, undepressed by admixture of an authentic sample.

Found%: Hg 56.54; 56.50
$(C_6H_5)_2Hg$. Calculated%: Hg 56.50

Ether was completely removed from the mother liquor under reduced pressure, and the oil so obtained was dissolved in an equal volume of methanol and added to a solution of 1.6 g of mercuric chloride in 20 ml of alcohol. Crystals of phenylmercury chloride separated and were filtered off; m.p. 252-253°. Methanol was completely removed from the filtrate under reduced pressure. From the oily residue chloroform precipitated a mixture of ethyl (chloromercuri)acetate and mercurous salts. This material was extracted with acetone, and evaporation of the extract yielded ethyl (chloromercuri)acetate, m.p. 64-66°.

Found%: Hg 61.79
$ClHgCH_2COOC_2H_5$. Calculated%: Hg 62.08

SUMMARY

1. It was shown that arylmercury hydroxides do not react with unsaturated hydrocarbons.

2. Arylmercury hydroxides react with vinyl ethers with formation of the diarylmercury together with mercuridiacetaldehyde or a mercuridialkanone. The reaction can be applied as a new method for the symmetrization of organomercury salts under mild conditions; it gives almost quantitative yields of diarylmercury.

3. Arylmercury hydroxides readily react with ketene diethyl acetal with formation of the diarylmercury and mercurated ethyl acetate.

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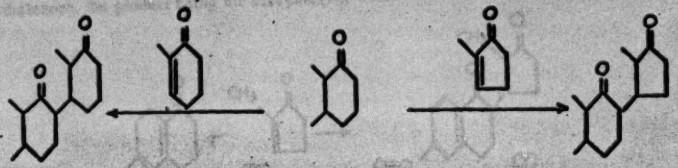
SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

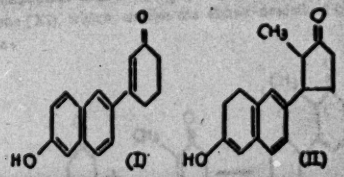
COMMUNICATION 36. CONDENSATION OF CYCLIC SATURATED KETONES WITH α,β-UNSATURATED CYCLIC KETONES

I. N. Nazarov, S. I. Zavyalov, and M. S. Burmistrova

In our laboratory we have recently [1] developed convenient methods for the preparation of α,β-unsaturated cyclic ketones, which we have used in numerous diene condensations and so have synthesized a variety of polycyclic compounds related to steroids. It was considered to be of interest to study also the Michael condensation of α,β-unsaturated cyclic ketones with saturated ketones with the object of preparing polycyclic ketones of the bicyclohexyl and cyclopentylcyclohexane series according to the schemes indicated:



As is well known, these classes of compounds include some synthetic estrogens, for example the tricyclic ketones (I) [3] and (II) [4].

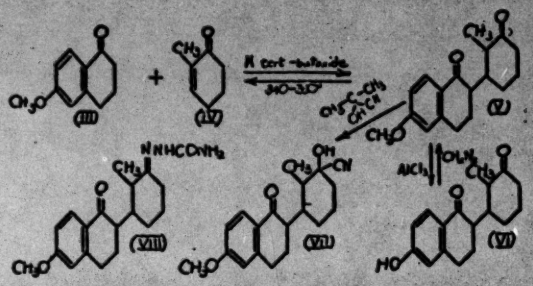


It was found that these condensations occur in quite satisfactory yields at room temperature in presence of one-third of an equivalent of potassium in a medium of tert-butyl alcohol and dioxane.

Reaction of 2-methyl-2-cyclohexen-1-one (IV) with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (III) gave about a 50% yield of a crystalline ketone which corresponded in elementary analysis and chemical properties to the normal condensation product (V).

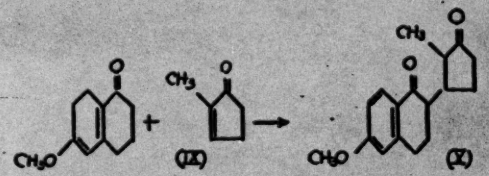
At 340-350° the diketone (V) decomposed into its original components, and when heated in the cold with excess of acetone cyanohydrin in presence of piperidine a 70% yield of the monocyanohydrin (VII) was formed (see scheme on top of following page); which is in accord with the known inertness of the carbonyl group of 3,4-dihydro-1(2H)-naphthalenone toward acetone cyanohydrin [5]. It is interesting to note that with excess of semicarbazide the diketone (V) again gives only a mono-derivative (VIII), the structure of which must be analogous to that of the monocyanohydrin (VII).

Demethylation of the diketone (V) with aluminum chloride in boiling xylene gave a 40% yield of the corresponding phenol (VI), which could be reconverted into the diketone (V) by the action of diazomethane.



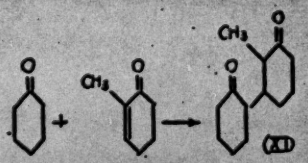
Although the phenol (VI) is very similar structurally to the physiologically active compounds (I) and (II), it showed no estrogenic activity when tested on rats.

It was found that 2-methyl-2-cyclopenten-1-one (IX) also combined with 3,4-dihydro-6-methoxy-1(2H)-naphthalenone, the product being the diketone (X), which was characterized as the monosemicarbazone:



When the diketone (X) was demethylated with the aid of aluminum chloride in xylene or hydrogen bromide in acetic acid, the product was a phenolic oil which we could not crystallize.

Condensation of cyclohexanone with 2-methyl-2-cyclohexen-1-one resulted in the formation of 2'-methyl-[bicyclohexyl]-2,3'-dione (XI), which, unlike the above-described condensation products (V) and (X), readily gave a disemicarbazone:



EXPERIMENTAL

Condensation of 3,4-Dihydro-6-methoxy-1(2H)-naphthalenone with 2-Methyl-2-cyclohexen-1-one. A solution of 6.8 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (III) (b.p. 135-138°/12 mm, m.p. 78-79°) [6] in 20 ml of dioxane was added to a stirred solution of potassium tert-butoxide prepared by dissolving 0.4 of potassium in 10 ml of tert-butyl alcohol, and then dropwise addition was made of 4.4 g of 2-methyl-2-cyclohexen-1-one (IV) (b.p. 56-57°/9 mm, n_D^{20} 1.4865. [1]. The mixture was set aside for three hours at room temperature and was then neutralized to Congo red with concentrated hydrochloric acid and evaporated to dryness under reduced pressure. The residue was treated with water and extracted with ether. Vacuum fractionation of the reaction product yielded 1 g of unchanged 3,4-dihydro-6-methoxy-1(2H)-naphthalenone and 7 g of an oil boiling at 200-215° (1 mm). Addition of ether to this oil precipitated the diketone (V), m.p. 115-116° (from aqueous methanol). The yield was 5 g (53% on the amount of the 3,4-dihydro-6-methoxy-1(2H)-naphthalenone that reacted).

	Found %:	C 75.12; 75.10; H 7.80; 7.94
$C_{18}H_{22}O_3$.	Calculated %:	C 75.4; H 7.7

After being washed with methanol, the monosemicarbazide melted with decomposition at 237-238°.

Found%: N 11.81; 11.89
$C_{19}H_{25}O_3N_3$. Calculated%: N 12.2

Thermal Decomposition of the Diketone (V). The above-described diketone (V) (0.5 g) was heated at 340-350° until distillation ceased (10-15 minutes). The distillate solidified almost completely. The product isolated was 0.1 g (33%) of 3,4-dihydro-6methoxy-1(2H)-naphthalenone (III).

Demethylation of the Diketone (V). A stirred mixture of 0.5 g of the diketone (V), 1 g of aluminum chloride, and 10 g of dry xylene was boiled for seven minutes. The reaction mixture was cooled and decomposed by addition of ice and dilute (1:1) hydrochloric acid. The precipitate that formed was dissolved in dilute caustic soda (2-5%), and after filtration of the solution the substance was reprecipitated with dilute hydrochloric acid. The product was 0.2 g (40%) of the monohydrate of the phenol (VI), m.p. 196-198° (from aqueous methanol).

Found%: C 70.43; 70.45; H 7.60; 7.63
$C_{17}H_{22}O_3H_2O$. Calculated%: C 70.4; H 7.6

After being washed with methanol, the monosemicarbazide melted with decomposition at 247-248°.

Found%: N 13.14; 13.25
$C_{18}H_{25}O_3N_3$. Calculated%: N 12.8

Treatment of the phenol (VI) with diazomethane in ether converted it into the original diketone (V).

Preparation of the Cyanohydrin of the Diketone (V). A mixture of 0.3 g of the diketone (V), 0.5 g of acetone cyanohydrin, one drop of piperidine, and 10 ml of ether was allowed to stand for one day at room temperature. The product isolated was 0.2 g of the cyanohydrin (VII), m.p. 165-168°. The mother liquor was evaporated to dryness under reduced pressure, and 0.5 g of acetone cyanohydrin and 10 ml of ether were added to the residue. After a time a further 0.05 g of the cyanohydrin (VII) was precipitated, the total yield being 0.25 g (70%).

Found%: C 73.00; 73.04; H 7.43; 7.60; N 4.61; 4.65
$C_{15}H_{23}O_3N$. Calculated%: C 72.8 H 7.4; N 4.5

Condensation of 3,4-Dihydro-6-methoxy-1(2H)-naphthalenone with 2-Methyl-2-cyclopenten-1-one. The procedure was the same as for the condensation with 2-methyl-2-cyclohexen-1-one. Reaction of 7 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone with 4.2 g of 2-methyl 2-cyclopenten-1-one (IX) (b.p. 52-53°/15 mm, n_D^{20} 1.4470) [1] yielded 4 g of the diketone (X), b.p. 195-201° (1.5 mm), n_D^{20} 1.5660. When the amount (1.9 g) of unchanged 3,4-dihydro-6-methoxy-1(2H)-naphthalenone was taken into account, it was found that the yield of the diketone (X) was 51%.

Found%: C 74.74; 74.6; H 7.44; 7.49
$C_{17}H_{20}O_3N_3$. Calculated%: C 75.0 H 7.3

After being washed with methanol, the monosemicarbazide melted at 217-218°.

Found%: N 12.56; 12.36
$C_{21}H_{23}O_3N_3$. Calculated%: N 12.8

Demethylation of the Diketone (X). A mixture of 0.5 g of the diketone (X) and 10 ml of a solution, saturated at 70°, of hydrogen bromide in glacial acetic acid was heated at 65-70° for five hours. The solution was evaporated to dryness under reduced pressure. The residue was dissolved in dilute alkali, the solution was filtered, and the reaction product was precipitated with dilute hydrochloric acid. The product was 0.3 g of a viscous noncrystallizing oil of phenolic character.

When the demethylation of the diketone (X) was effected with the aid of aluminum chloride in xylene, we were again unable to isolate a crystalline phenol.

Condensation of Cyclohexanone with 2-Methyl-2-cyclohexen-1-one. The condensation was carried out in the manner described above. Reaction between 2 g of cyclohexanone and 2.2 g of 2-methyl-2-cyclohexen-1-one yielded 2.5 g (59%) of 2'-methyl-[bicyclohexyl]-2,3'-dione (XI), b.p. 142-145° (1.5 mm), n_D^{20} 1.5115

Found%: C 74.62; 74.56; H 9.48; 9.66
$C_{13}H_{20}O_2$. Calculated%: C 74.9 H 9.6

After being washed with methanol, the disemicarbazide melted at 237-238° (with decomposition).

Found%: N 25.72; 25.50

$C_{18}H_{26}O_2N_6$. Calculated%: N 26.1

In conclusion we express our thanks to Prof. M. D. Mashkovsky for estrogenic-activity tests on the diketone (VI).

SUMMARY

[1] Diketones of the bicyclohexyl and cyclopentylcyclohexane series were synthesized by the Michael condensation of cyclic ketones with α,β-unsaturated cyclic ketones.

[2] When 3,4-dihydro-6-methoxy-1-(2H)-naphthalenone (III) was condensed with 2-methyl-2-cyclohexen-1-one (IV) and with 2-methyl-2-cyclopenten-1-one (IX) in presence of potassium tert-butoxide in tert-butyl alcohol and dioxane, the respective products, obtained in about 50% yield, were the diketones (V) and (X). Condensation cyclohexanone with 2-methyl-2-cyclohexen-1-one gave the diketone (XI) in 59% yield.

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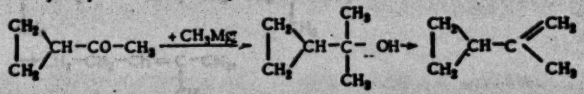
• T.p. = C. B. Translation pagination

HYDROGENATION OF ISOPROPENYLCYCLOPROPANE IN PRESENCE OF PALLADIUM BLACK

B. A. Kazansky, M. Yu. Lukina, A. I. Malyshev, V. T. Aleksanyan, and Kh. E. Sterin

As we wished to study the physical properties and chemical behavior of alkylcyclopropanes having a branched side chain, we decided to synthesize such compounds from the corresponding tertiary alcohols of the cyclopropane series. Such alcohols are readily prepared from alkyl cyclopropyl ketones, and they readily give the corresponding alkenylcyclopropanes by dehydration, for example:



We hoped that we should be able to obtain the required alkylcyclopropanes by hydrogenating the double bond of unsaturated hydrocarbons obtained in this way, but our attempts to hydrogenate one of these compounds— isopropenylcyclopropane — in presence of palladium black at ordinary temperature and pressure did not give the desired result: addition of two molecules of hydrogen occurred with formation of 2-methylpentane. The formation of this paraffin — product of the hydrogenolysis of the three-membered ring at the bond adjacent to the substituent — stands in conflict with several reported experimental facts relating to the hydrogenolysis of alkylcyclopropanes. Thus, Kizhner [1], and later Rozanov [2], found that in the hydrogenolysis of alkylcyclopropanes over nickel at 150° in a flow system, hydrogen adds at the bond lying opposite to the carbon carrying the substituent, or, in more general terms, hydrogen adds to the most hydrogenated carbon atoms.

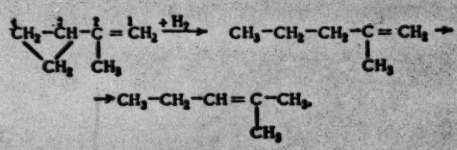
In our investigations [3, 4] on the catalytic hydrogenation of alkylcyclopropanes in the vapor phase at atmospheric pressure in presence of platinized charcoal, this law was fully confirmed. It was confirmed also in the investigations of Boord and coworkers [5], who carried out the hydrogenolysis of alkylcyclopropanes over a nickel catalyst under different conditions, the hydrogen being under pressure. It should be noted these authors hold the view — which is contrary to our observations [4] — that the three-membered cycle has considerable stability, fairly severe conditions being required for the rupture of C—C linkages of the ring. For example, they carried out the hydrogenolysis of isopropylcyclopropane (with formation of 2,3-dimethylbutane) at 150-200° and 87 atm. However, in an attempt to hydrogenate the double bond of isopropenylcyclopropane selectively under milder conditions (37°, 56 atm), these authors obtained isopropylcyclopropane together with an appreciable amount of 2-methylpentane. In explanation of this fact they suggested that the formation of the second substance was due to the conjugation of the double bond of isopropenylcyclopropane with the three-membered ring; this suggestion was not checked experimentally. Later, Slabey [6] showed that by the use of baryta-promoted copper chromite catalyst at 100-130° and 105-140 atm it is possible to hydrogenate the double bond of isopropenylcyclopropane without touching the C—C bonds of the ring.

Having obtained 2-methylpentane by the hydrogenation of isopropenylcyclopropane in presence of palladium, we considered it essential to determine the cause of the anomalous course of the reaction. We decided, therefore, to isolate the intermediate hydrogenation products, carrying out the reaction under the same conditions but interrupting it as soon as the absorption of one molecular proportion of hydrogen was complete. The results of the fractionation of the catalyzate led us to suppose that the mixture contained not only isopropane and 2-methylpentane, but also 2-methylpentenes. However, the components of the mixture were so similar in boiling point that we were unable to isolate them in pure state. We therefore determined the composition of the catalyzate from Raman spectra.

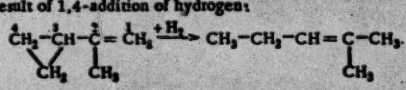
The spectrum of isopropenylcyclopropane was not known, and the data in the literature on the spectra of 2-methyl-1-pentene and 2-methyl-2-pentene [7, 8] did not appear to be sufficiently reliable. It was therefore necessary to synthesize the last two hydrocarbons and to determine the spectra of all three compounds, expressing the intensities of the lines in the accepted cyclohexane scale. It was indeed found that, for example, in 2-methyl-1-pentene the frequency of the double bond is 1650 cm^{-1}, and not 1663 cm^{-1} [8]. Investigation of the spectra of the catalyzate showed that the mixture of hydrocarbons obtained as a result of incomplete hydrogenation consisted

of unchanged isopropenylcyclopropane, 2-methyl-2-pentene, and, in smaller amount, 2-methyl-1-pentene. In addition, a small amount of 2-methylpentane was found. No isopropylcyclopropane could be detected in the catalyzate by spectrum analysis. This indicates that the double bond of isopropenylcyclopropane does not undergo selective hydrogenation, the final reaction product – 2-methylpentane – being formed by the hydrogenation of 2-methylpentenes formed as intermediate products. The formation of 2-methylpentenes can readily be explained when we regard isopropenylcyclopropane as a conjugated system in which the three-membered ring is conjugated with the double bond.

The formation of 2-methyl-2-pentene could then be either the result of the hydrogenolysis of the three-membered ring at a bond adjacent to the substituent, i.e. 3,4-addition of hydrogen with subsequent partial isomerization of the resulting 2-methyl-1-pentene into 2-methyl-2-pentene:



or the result of 1,4-addition of hydrogen:



In order to determine the mechanism with greater precision it was necessary to check whether or not the isomerization of 2-methylpentenes with displacement of the double bond from position 1 to 2 and vice versa actually occurs under the hydrogenation conditions. We therefore took our synthetic 2-methyl-1-pentene and 2-methyl-2-pentene and shook them with palladium black, shaking being stopped when only 0.2 of a molecular proportion of hydrogen had been absorbed so that olefins formed by double-bond displacement should, in the main, be preserved in the catalyzate. These experiments showed that, under such conditions, these methylpentenes do in fact isomerize into one another, giving mixtures of 2-methyl-2-pentene and 2-methyl-1-pentene identical in composition, the first compound predominating.

As a special experiment showed, isopropenylcyclopropane itself is not isomerized when its alcoholic solution is shaken with reduced palladium black.

The above facts enable us to conclude that, in hydrogenation under the conditions described above, conjugation does indeed occur between the double bond and the three-membered cycle in isopropenylcyclopropane with consequent weakening of the C–C bond of the ring which is adjacent to the substituent. The fact that isopropylcyclopropane is not formed, or is formed only in insignificant amount, in the hydrogenation of isopropenylcyclopropane indicates that hydrogen adds more readily to a three-membered ring conjugated with a double bond than to the double bond itself.

EXPERIMENTAL

Isopropenylcyclopropane was prepared by the dehydration of 1-cyclopropyl-1-methylethanol with the aid of a few drops of concentrated sulfuric acid. After distillation through a column the hydrocarbon had b.p. 70.5° (760 mm); n_D^{20} 1.4255; d_4^{20} 0.7517 •.

$\Delta\nu$ (cm^{-1}): 234 (2 b), 268 (36 b), 294 (0), 315 (1), 343 (0), 359 (0), 394 (16), 415 (27), 474 (55, sh), 587 (18 diff. background) 531 (12), 695 (12), 714 (41, sh), 729 (19), 797 (6), 818 (25, b), 890 (60), 900 (30, b) 933 (0), 932 (37), 995 (9, sh) 1020 (17) 1035 (3), 1049 (3, dif), 1089 (15, dif), 1100 (14, dif), 1169 (3, dif), 1192 (110, b, doublet), 1225 (5, dif), 1238 (6 dif) 1293 (16 sh), 1318 (2), 1340 (4, dif), 1369 (4, dif), 1391 (50, b, doublet), 1403 (10, background), 1428 (64, background), 1459 (43 background), 1503 (2), 1635 (114, sh), 1649 (90, sh), 2854 (10, background) 2870 (10, background), 2898 (20 dif), 2917 (45, sh), 2938 (10, background), 2973 (20 dif), 2988 (60, sh), 3013 (140, b, doublet), 3083 (60, b, doublet).

2-Methyl-1-pentene was prepared in admixture with 2-methyl-2-pentene by the dehydration of 2-

• Data from the literature was given in Table 1 for all of the hydrocarbons synthesized.

methyl-2-pentanol with the aid of iodine. The hydrocarbons were separated by distillation through a 100-plate laboratory column.

2-Methyl-1-pentene: b.p. 61.4° (760 mm); n_D^{20} 1.3918; d_4^{20} 0.6802.

$\Delta\nu$ (cm^{-1}): 199 (6,dif), 267 (1), 292 (0), 327 (7 dif), 349 (7,dif), 372 (0), 400 (20b), 414 (1,dif), 428 (3,dif), 447 (5,dif), 469 (1), 497 (4,dif), 527 (14,sh), 538 (3), 592 (0), 622 (0), 676 (1), 703 (12), 738 (17,sh), 768 (1), 794 (1), 818 (24,sh), 826 (31,sh), 865 (1,dif), 890 (18), 899 (14), 939 (1), 964 (3), 978 (1) 995 (9), 1027 (3 dif), 1046 (14,b), 1079 (1), 1102 (17,b), 1149 (1), 1175 (1), 1200 (1), 1215 (12,dif), 1225 (3,dif), 1259 (3), 1271 (0), 1301 (7,dif), 1327 (3,dif), 1351 (1), 1383 (22,b), 1411 (39,b), 1428 (46,b), 1453 (34,b), 1651 (76,sh), 2818 (10,dif), 2843 (30,dif background), 2873 (150,sh80), 2888 (30,background), 2902 (60,background), 2914 (170), 2938 (130), 2965 (80,dif), 2984 (80,dif), 3001 (30,dif), 3020 (5), 3077 (25,b).

2-Methyl-2-pentene: b.p. 66.9° (760 mm); n_D^{20} 1.4004; d_4^{20} 0.6882.

$\Delta\nu$ (cm^{-1}): 260 (0), 359 (17,dif), 406 (4,dif), 413 (4,dif), 444 (0), 472 (110,dif), 514 (13), 717 (1), 746 (10), 764 (2,dif), 818 (21), 833 (15,dif), 875 (0), 908 (9,dif), 929 (0,dif), 956 (3,dif), 986 (0), 1008 (7,dif), 1063 (34), 1084 (2,dif), 1121 (5, doublet), 1149 (4,dif), 1167 (4,dif), 1203 (3 dif), 1263 (8), 1305 (19,sh), 1353 (10), 1382 (43,sh) 1439 (15,dif,background), 1455 (53,b), 1478 (4,dif), 1525 (5), 1677 (145), 2727 (10,dif), 2856 (80,dif), 2876 (100 dif), 2889 (40,dif,background), 2913 (160,dif), 2967 (100,dif), 2987 (20,dif), 3035 (10).

The Catalyst was palladium black, prepared from palladium chloride by Zelinsky's method [9].

Hydrogenation was carried out at 18-20° in a 100-ml hydrogenation flask of the usual type. Distilled ethanol (40 ml for each experiment) and electrolytic hydrogen were used, and a fresh portion of catalyst (0.4 g) was taken for each experiment. The hydrogenation product was distilled off as an azeotropic mixture with alcohol through a column having a glass packing; it was then washed, dried, and fractionated through a 40-plate column having a copper packing. In all fractionations 7 ml of heptane (n_D^{20} 1.3877), was added as a displacing agent.

Isomerization was carried out under the same conditions as hydrogenation. In the case of isopropenylcyclopropane it was carried out in absence of hydrogen, and in the case of the methylpentenes it was carried out in presence of hydrogen, 20% of the amount necessary for hydrogenation being allowed to add. The catalyzate was separated as in the case of hydrogenation.

TABLE 1

Hydrocarbon	B.p. (°C,760 mm)	n_D^{20}	d_4^{20}
Isopropenylcyclopropane [6]	70.33	1.42550	0.75153
Isopropylcyclopropane [6]	58.37	1.38639	0.69829
2-Methylpentane [10]	60.271	1.37145	0.65315
2-Methyl-2-pentene [10]	67.29	1.4004	0.6863
2-Methyl-1-pentene [10]	60.7	1.3915	0.6817

Data from the literature on isopropenylcyclopropane and hydrocarbons that can be obtained when it is hydrogenated are given in Table 1.

Hydrogenation

Experiment 1. The isopropenylcyclopropane (11.5 g, i.e. 15.4 ml) absorbed 6230 ml of hydrogen *. The theoretical amount of hydrogen, corresponding to the addition of two molecular proportions, is 6270 ml. The catalyzate amounted to 11.2 g (17.1 ml). The fractionation results are given in Table 2.

On the basis of the constants given in Table 2, the product of the addition of two molecular proportions of hydrogen to isopropenylcyclopropane is 2-methylpentane.

Experiment 2. The amount of isopropenylcyclopropane taken was 18.2 g (24.4 ml), the theoretical two molecular proportions of hydrogen being 9930 ml. The amount of hydrogen that added was 5500 ml, i.e. somewhat more than one molecular proportion, and 16.3 g (23.8 ml) of catalyzate was obtained. The results of the

* In all experiments the volume of hydrogen is adjusted to normal conditions.

fractionation are given in Table 3.

TABLE 2

Fraction	B.p. (°C, 760 mm)	n_D^{20}	d_4^{20}	Aniline point	Weight (g)	Volume (ml)
I	60.0–60.3	1.3717	0.6537	—	1.9	2.6
II	60.3	1.3716	0.6534	73.8	6.5	10.0
III	60.3	1.3716	0.6534		2.2	3.4
Losses					0.6	1.1

TABLE 3

Fraction	Amount (ml)	Amount (g)	B.p. (°C, 760 mm)	n_D^{20}	d_4^{20}
I–II	2.3	1.6	58.4–60.0	1.3840	0.6683
III	3.0	2.1	60.0–61.8	1.3856	0.6717
IV	3.5	2.3	61.8–64.0	1.3908	0.6787
V	2.0	1.5	64.0–66.8	1.3962	0.6844
VI	3.0	2.1	66.8–67.5	1.3998	0.6888
VII	4.5	3.2	67.5–67.6	1.4009	0.6919
VIII	2.7	1.9	67.6–69.4	1.4088	0.7103
IX	0.6	0.5	69.4–70.0	1.4128	
Losses	—	1.1			

On the basis of the data in Table 3, the catalyzate may contain all of the hydrocarbons listed in Table 1. Fractions V-VII consist essentially of 2-methyl-2-pentene.

Experiment 3. The amount of isopropenylcyclopropane taken was 22.3 g (30.0 ml), which theoretically requires 12.160 ml of hydrogen for complete hydrogenation. The amount that actually added was 6070 ml, and 20.8 g (31.0 ml) of catalyzate was obtained. The fractionation results are given in Table 4 and Fig. 1.

TABLE 4

Fraction	Amount (ml)	Amount (g)	B.p. (°C, 760 mm)	n_D^{20}	d_4^{20}
I	2.5	1.6	58.0–60.0	1.3855	0.6668
II	6.0	4.0	60.0–62.1	1.3882	0.6735
III	4.0	2.8	62.1–65.0	1.3933	0.6809
IV	5.0	3.7	65.0–67.3	1.3998	0.6857
V	7.0	4.9	67.3–67.4	1.4018	0.6902
VI	4.0	3.0	67.4–69.8	1.4108	0.7181
Losses		0.8			

As in Experiment 2, mixtures of hydrocarbons were obtained with a predominance of 2-methyl-2-pentene in Fractions IV and V. In order to isolate 2-methyl-2-pentene in a purer state, Fractions V-VII from Experiment 2 and Fractions IV and V from Experiment 3 were combined and refractionated through a column. Altogether, 15.0 g (21.6 ml) of hydrocarbon mixture was taken for fractionation. The results of the fractionation are given in Table 5.

Fractions II and III, according to their constants, are 2-methyl-2-pentene. For analysis with the aid of Raman spectra the following samples are used:

Sample I (6.0 g) - a mixture of Fractions I-IV from Experiment 2 (see Table 3).

Sample II (12.3 g) - a mixture of Fractions I-III from Experiment 3 (see Table 4) and Fraction I from the refractionation (see Table 5).

Sample III (5.9 g) - a mixture of Fractions II and III from the refractionation (see Table 5).

TABLE 5

Fraction	Amount		B.p. (°C,760 mm)	n_D^{20}	d_4^{20}
	(ml)	(g)			
I	5.5	3.9	63.4–67.1	1.3980	0.6853
II	4.0	2.7	67.1–67.2	1.4008	0.6881
III	4.5	3.2	67.2–67.3	1.4009	0.6889
Residue	6.6	4.6		1.4065	0.7035
Losses	1.0	0.6			

Sample IV (8.1 g)– a mixture of Fraction IX from Experiment 2 (see Table 3), Fraction VI from Experiment 3 (see Table 4), and the residue from the refractionation (see Table 5).

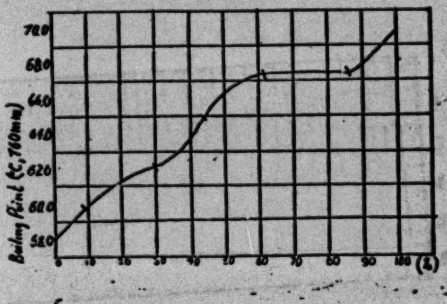


Fig. 1. Fractionation curve of the catalyzate from Experiment 3.

The Raman spectra of Samples II, III and IV are given in Fig. 2; the spectrum of Sample I differed little from that of Sample II and is therefore not given. On the basis of the spectrographic investigation of Samples I-IV, the following tentative values were calculated for the contents of hydrocarbons in the catalysis products:

2-Methyl-1-pentene	~ 30%
2-Methyl-2-pentene	~ 50%
Isopropenylcyclopropane	~ 8%
2-Methylpentane	~ 12%

We hope to obtain more precise values in a further investigation.

Isomerization

Experiment 1. Shaking of 15.0 g (20.0 ml) of isopropenylcyclopropane with reduced catalyst was continued for 16 hours. The product isolated was 13.7 g (18.4 ml) of a hydrocarbon having n_D^{20} 1.4253; d_4^{20} 0.7513. Judging from these constants, the isopropenylcyclopropane remained unchanged.

Experiment 2. 2-Methyl-2-pentene, amounting to 19.8 g (28 ml), was taken, and 1030 ml of hydrogen was allowed to add, the theoretical amount for complete hydrogenation being 5270 ml. The catalyzate (17.5 g; 25.6 ml) had b.p. 60.0 – 65.5° (749.2 mm).

Experiment 3. 2-Methyl-1-pentene, amounting to 10.5 g (15.4 ml), was taken, and 660 ml of hydrogen was allowed to add, the theoretical amount for complete hydrogenation being 2790 ml. The catalyzate (8.2 g; 12.0 ml) had b.p. 60.0-65.0° (749.2 mm).

The catalyzates from Experiments 2 and 3 were analyzed with the aid of Raman spectra. The spectra of the isomerization products obtained in these experiments are quite identical; they are shown in Fig. 3.

SUMMARY

1. It was found that in the hydrogenation of isopropenylcyclopropane in alcohol solution in presence of palladium black at room temperature and atmospheric pressure two molecular proportions of hydrogen add with

Fig. 2. Raman spectra: 1) 2-methyl-1-pentene; 2) Sample II; 3) 2-methyl-2-pentene; 4) Sample III; 5) Sample IV; 6) isopropenylcyclopropane.

Fig. 3. Spectra of isomerization products: 1) 2-methyl-1-pentene; 2) 2-methyl-2-pentene.

formation of 2-methylpentane.

2. It was shown that the hydrogenation of isopropenylcyclopropane proceeds through the intermediate formation of 2-methyl-1-pentene and 2-methyl-2-pentene.

3. It was found that, under the hydrogenation conditions used, reversible isomerization of 2-methyl-2-pentene into 2-methyl-1-pentene occurs.

4. It was shown that isopropenylcyclopropane remains unchanged when shaken for a long time with reduced palladium black.

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HIGH-TEMPERATURE REACTIONS OF PROPYL- AND ISOPROPYL-BENZENES OVER A NICKEL-ALUMINA CATALYST IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

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Various investigations have been devoted to the contact-catalysis reactions of aromatic hydrocarbons [1-3], and these have been mainly concerned with the study of reactions occurring at atmospheric pressure in presence of oxide catalysts. At the present time, however, there is much interest in the behavior of benzene homologs under the influence of oxide-metal catalysts in presence of hydrogen at high pressure [4].

We have already [5-7] published the results of investigations on the contact-catalysis reactions of some individual cycloalkanes, alkanes, and simple aromatic hydrocarbons at high temperature in presence of hydrogen at high pressure. On the basis of the experimental results then obtained we advanced a hypothesis concerning the character and direction of the reactions occurring over platinized alumina in presence of hydrogen at high pressure.

As early as 1934, one of us in collaboration with Zelinsky [8] showed that at 350° a nickel-alumina catalyst not only has a marked dehydrogenating action, but also has the ability to bring about a synthetic process: catalytic methylation of cyclic hydrocarbons by methylene radicals formed under the reaction conditions.

When planning the present investigation, we started from the assumption that the use of a high pressure of hydrogen in the catalysis of aromatic hydrocarbons would increase the stability of the catalyst and enable us to obtain a clearer picture of the synthetic processes of the type noted in earlier work.

EXPERIMENTAL

We investigated the behavior of the two isomers - propyl - and isopropyl-benzenes - in contact with finely dispersed nickel carried on activated alumina. In the catalysts used in the investigation the contents of active metal were 10, 20, and 30%. Their hydrogenating and dehydrogenating properties were first determined refractometrically for the transformations of benzene at 180° and of cyclohexane at 300°. It was found that in presence of the 20% or 30% nickel-alumina catalyst benzene was almost completely hydrogenated to cyclohexane under these conditions and cyclohexane was dehydrogenated to benzene to the extent of 98%.

After fractionation through a 42-plate column, the propylbenzene had the following properties: b.p. 159-159.7° (759 mm); n_D^{20} 1.4920; d_4^{20} 0.8621. The isopropylbenzene had b.p. 153.9-152.0° (758 mm); n_D^{20} 1.4915; d_4^{20} 0.8623.

These hydrocarbons were brought into contact with catalyst in a flow-type apparatus at a space velocity of 0.8 hr^{-1}, the molar ratio of hydrogen to hydrocarbon being about 5:1 [9]. The liquid catalysis products were investigated by means of precision rectification, chromatographic adsorption, and Raman spectra. The gaseous products were analyzed in an Orsat-Lunge apparatus. For each experiment 100 g of substance was taken.

Catalysis of Propylbenzene

Propylbenzene was brought into contact with nickel catalysts at 460-465° at hydrogen pressures of 25 and 50 atm. The catalysis results are given in Table 1.

As will be seen from Table 1, a change in the content of finely dispersed nickel in the catalyst from 30 to 10% results in a lowering of the extent of conversion of the propylbenzene by 10%. A detailed investigation was made on the catalyzate obtained by treating propylbenzene with nickel-alumina containing 20% Ni at 465° and 25 atm hydrogen pressure. For fractionation through the 42-plate column, 100 ml (86.6 g) of this catalyzate (n_D^{20} 1.4975; d_4^{20} 0.8661.) was taken. The fractionation results are given in Table 2.

* Deceased.

TABLE 1

Conditions in Experiments with Propylbenzene and the Properties of the Catalyzates

Ni content of catalyst (%)	Experimental conditions		Yield of catalyzate	Properties of catalyzates		Extent of conversion of original hydrocarbon (%)
	Pressure (atm)	Temperature (°C)		n_D^{20}	d_4^{20}	
30	25	465	78.5	1.4975	0.8593	97.6
	50	460	77.3	1.4970	0.8595	97.5
20	25	465	80.1	1.4975	0.8661	96.5
10	25	465	78.9	1.4956	0.8623	81.5

TABLE 2

Fractional Composition of Propylbenzene Catalyzate and Properties of the Fractions.

Fraction no.	Boiling limits (°C, 756 mm)	Yield (g)	n_D^{20}	d_4^{20}	Yield on amount of mixture taken for fractionation (% by weight)
I	60.5–73.6	4.8	1.4450	0.7345	5.6
II	73.6–78.9	0.8	1.4780	—	0.8
III	78.9–80.1	47.3	1.4985	0.8732	55.0
IV	80.1–109.5	0.7	1.4975	—	0.7
V	109.5–110.9	10.8	1.4965	0.8667	12.5
VI	110.9–133.7	0.8	1.4940	—	0.8
VII	133.7–136.5	7.9	1.4957	0.8673	9.2
VIII	136.5–149.0	2.8	1.4965	0.8669	3.2
IX	149.0–155.6	1.5	1.4915	0.8621	1.6
X	155.6–159.8	3.0	1.4918	0.8620	3.5
Residue		5.4	1.5015	—	6.2

It will be seen from the results given in Table 2 that Fraction I, judging from its properties, contains – apart from traces of benzene, which were detected by the formolite reaction – some alkanes and cycloalkanes. Removal of benzene from this fraction by chromatographic adsorption resulted in the separation of 4.8 ml of dearomatized fraction having n_D^{20} 1.4085 and d_4^{20} 0.7128. Optical analysis of this showed the presence of methylcyclopentane (about 60%), cyclohexane (about 15%), and hexane isomers (qualitatively). There was not enough of Fraction II for investigation.

The properties of Fraction III (78.9-80.1°) gave us reason to suppose that it contained benzene and some cyclohexane. In order to verify this supposition, part of the fraction was subjected to Zelinsky dehydrogenational catalysis. Platinized charcoal (4.5% Pt) was taken as catalyst, and the fraction was passed over this at 300-305° until there was no further change in refractive index (three successive passages). The catalyzate so obtained had n_D^{20} 1.5005 and d_4^{20} 0.8765. It follows that, in addition to benzene, Fraction III contained about 2% of cyclohexane [10]. Owing to the small amounts of material available, the intermediate fractions IV and VI were not investigated. Fraction V (109.5-110.9°) corresponded in its properties to almost pure toluene. Fraction VII (133.7-136.5°) was ethylbenzene. In the product obtained by permanganate oxidation of a small portion of this fraction [11] only benzoic acid, m.p. 120.8°, was found.

In order to determine the structures of the xylenes present in Fraction VIII (136.5-149.0°), it was subjected to Ullmann oxidation [11]. The resulting acids were separated by the method described by Moldavsky and coworkers [12]. From the mixture of acids (3.6 g), 0.4 g of benzoic acid (m.p. 120.8°), 1.3 g of isophthalic acid, 1.5 g of terephthalic acid, and 0.4 g of phthalic acid (m.p. 190°) were isolated. The isophthalic and terephthalic acids were converted into their methyl esters, which melted at 65° and 140°, respectively.

Fraction IX (149.0-155.6°) corresponded in properties to isopropylbenzene. The permanganate oxidation product of this fraction was found to be benzoic acid (m.p. 121°). Fraction X (155.6-159.8°) was mainly unchanged propylbenzene.

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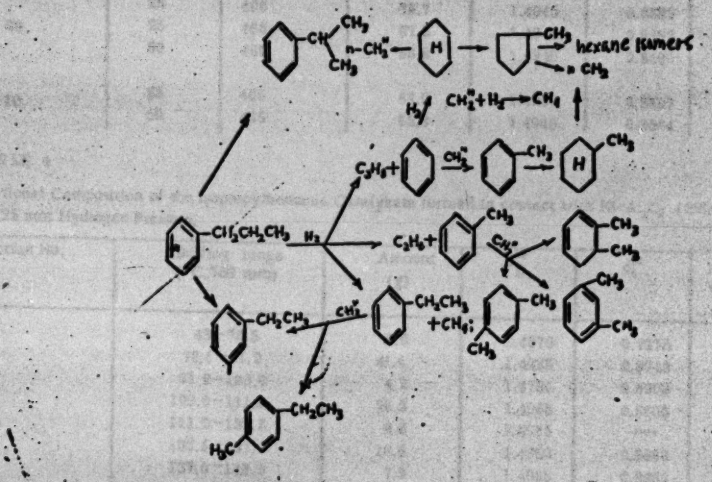
The residue (5.4 g) from the fractionation of the catalyzate was separated into the following fractions by distillation at 759 mm from a small flask attached to a fractionating column:

Fraction I	b.p. 159.8–169.8°;	3 g;	n_D^{20} 1.4920;	d_4^{20} 0.8619
Fraction II	b.p. 169.8–176.0°;	1.2 g;	n_D^{20} 1.4997;	d_4^{20} 0.8720
Fraction III	b.p. 176.0–184.0°;	0.7 g;	n_D^{20} 1.5447;	

Judging from its properties, Fraction I of this residue consisted essentially of unchanged propylbenzene. Oxidation of Fraction II yielded a mixture of phthalic acids (1.7 g) in which only isophthalic (0.8 g) and terephthalic (0.7 g) were identified, indicating the presence in the fraction of isomeric m- and p-dialkylbenzenes (probably ethyltoluenes).

On the basis of this investigation of the chemical composition of catalyzate fractions, we may present the following scheme of the transformations of propylbenzene under the conditions of our experiments:



Catalysis of Isopropylbenzene

The transformations of isopropylbenzene were investigated at 350°, 400°, and 465°, other conditions being the same. The results are given in Table 3.

It follows from the data given in Table 3 that rise of temperature from 350° to 465° results in a considerable increase in the yield of the products of complete and partial dealkylation of isopropylbenzene.

Reduction of the nickel content of the catalyst from 30% to 10% causes a comparatively small lowering of the degree of dealkylation of the isopropylbenzene. Increase of pressure from 25 to 50 atm at 465° has substantially no effect on the extent of conversion. A detailed investigation was made on the catalyzate obtained in the experiment carried out at 465° and 25 atm with a space velocity of 0.8 hr^{-1} over a nickel-alumina catalyst containing 20% Ni. The results of an analytical fractionation of 150 ml of the catalyzate through the 42-plate column are given in Table 4.

The properties of Fraction I (48–78.5°) gave us reason to suppose that, apart from benzene, it contained alkanes and cycloalkanes. After chromatographic removal of benzene, the dearomatized fraction (5.3 ml; n_D^{20} 1.4121 and d_4^{20} 0.7584) was analyzed optically. It was thus shown that this part of the fraction contained 65% of methylcyclopentane ($\Delta\nu$, cm^{-1}: 534, 845, 890, 1085, and others) and 30% of cyclohexane ($\Delta\nu$, cm^{-1}: 800, 1027, 1267, and others); hexane isomers were also detected qualitatively.

TABLE 3

Conditions in Experiments with Isopropylbenzene and the Properties of the Catalyzates

Ni content of catalyst (%)	Experimental conditions		Yield of catalyzate (%)	Properties of catalyzates		Extent of conversion of original hydrocarbon(%)
	Pressure (atm)	Temperature (°C)		n_D^{20}	d_4^{20}	
30	25	350	86.5	1.4946	0.8611	28.5
	25	400	83.4	1.4955	0.8625	49.5
	25	465	68.1	1.4965	0.8620	98.0
	50	465	67.6	1.4950	0.8598	97.5
20	25	400	78.7	1.4945	0.8589	39.3
	25	465	67.3	1.4945	0.8593	97.0
	50	465	66.8	1.4940	0.8590	96.5
10	25	465	68.9	1.4950	0.8597	91.3
	50	465	65.3	1.4945	0.8584	93.6

TABLE 4

Fractional Composition of the Isopropylbenzene Catalyzate formed in contact with Ni-Al_2O_3 (20% Ni) at 465° and 25 atm Hydrogen Pressure.

Fraction No.	Boiling range (°C, 758 mm)	Amount (g)	n_D^{20}	d_4^{20}	Yield on mixture taken for fractionation (%)
I	48–78.5	6.9	1.4670	0.7975	5.3
II	78.5–81.2	41.4	1.4985	0.8743	31.9
III	81.2–109.0	4.0	1.4780	0.8003	3.0
IV	109.0–111.0	26.3	1.4965	0.8665	20.2
V	111.0–133.5	0.8	1.4965	—	0.2
VI	133.5–137.0	16.6	1.4960	0.8668	12.8
VII	137.0–148.0	7.9	1.4965	0.8663	6.1
VIII	148.0–156.0	1.9	1.4925	0.8621	1.4
IX	156.0–159.8	3.9	1.4920	0.8619	3.0
X	159.8–164.0	7.4	1.4968	0.8670	5.7
XI	164.0–178.3	5.5	1.4945	0.8719	4.2
Residue		6.5	—	—	5.0

The properties of Fraction II (78.5-81.2°) gave us reason to suppose that it contained not only benzene, but also cyclohexane. In order to verify this supposition, part of the fraction was subjected to dehydrogenational catalysis in presence of platinized charcoal (4% Pt). After dehydrogenation the catalyzate consisted almost entirely of benzene. According to Zelinsky and Pavlov's curve [10], there must have been about 2.5% of cyclohexane in this fraction. Confirmation of the presence of cyclohexane in this fraction was obtained also from Raman spectra.

Aromatic hydrocarbons were removed from the intermediate Fraction III (81.2-109.0°), and it was then analyzed by the Raman spectrum method. Methylcyclohexane (about 70%) and heptane isomers (qualitatively) were detected in the dearomatized fraction.

Fraction IV (109-111.0°) corresponded in properties to almost pure toluene.

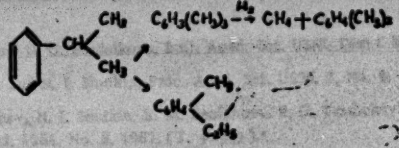
The intermediate Fraction V (111.0-133.5°) was not investigated owing to the smallness of the amount, but Fraction VI, judging from its properties, consisted essentially of ethylbenzene together with some m- and p-xylenes. Fraction VII (137-148.0°) was subjected to optical analysis. The results showed that in this xylene fraction there was about 10% of ethylbenzene ($\Delta\nu$ cm^{-1} : 159, 622, 771, 969, 1005, 1050, and others), 60% of m-xylene (230, 295, 540, 725, 1000, 1250, 1379, 1613), 15% of p-xylene (313, 460, 645, 829, 1183, 1205, 1379, 3054, and others), and 10% of o-xylene (179, 580, 735, 1054, 1223, 1384, 1609); in addition, it was established qualitatively

that a C_5 cyclopentane derivative was present in this fraction. Fraction VII (148-156°) was close to the original isopropylbenzene in properties. Fraction IX contained mainly propylbenzene, probably formed by the isomerization of isopropylbenzene; only benzoic acid (m.p. 120.8°) was found in its permanganate oxidation product. Fractions X and XI were subjected to optical analysis. Fraction X contained about 40% of propylbenzene, about 40% of p-ethyltoluene, and 20% of m-ethyltoluene; also, the presence of a small amount of trimethylbenzenes was established qualitatively.

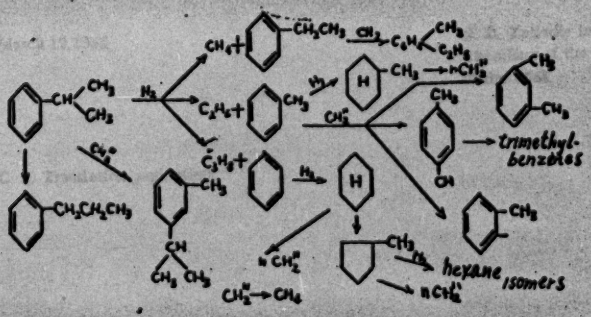
It was shown that Fraction XI consisted largely of p-isopropyltoluene, but meta derivatives of propylbenzene were also present.

The investigation of the isopropylbenzene catalyzate showed that the main reaction under the given conditions was partial and complete dealkylation of isopropylbenzene with formation of benzene (32%), toluene (20.2%), and ethylbenzene (12.8%). Simultaneously with this main reaction, other transformations also occurred: hydrogenation of the benzene nucleus to the cyclohexane ring, contraction of this ring to a five-membered ring, hydrogenolysis of the five-membered ring with formation of alkanes, and partial isomerization of isopropylbenzene into propylbenzene.

The presence in the catalyzate of xylenes and trimethylbenzenes may be explained by methylation of the benzene nucleus by methylene radicals, which, as we have suggested previously, are probably formed by the decomposition (at the surface of the nickel-alumina catalyst of cycloalkanes that are formed in the process. This explanation, however, is not the only possible one, for we cannot exclude the possibility that isopropylbenzene may isomerize to trimethylbenzene under our conditions and that hydrogenolysis of a methyl group may then occur:



Thus, the composition of the mixture of hydrocarbons formed as a result of the catalytic treatment of isopropylbenzene indicates the great variety of the reactions occurring under conditions of high temperature and high pressure of hydrogen. These reactions probably proceed in accordance with the following scheme:



SUMMARY

1. The contact-catalysis transformations of propyl- and isopropyl-benzenes were investigated at a nickel-alumina catalyst at various temperatures (350-465°) and at hydrogen pressures of 25 and 50 atm.

2. It was found that, under these catalysis conditions at 465°, about 98% of the original hydrocarbon undergoes far-reaching transformations.

3. It was shown that the main reaction in the transformations of propyl- and isopropyl-benzenes is the

hydrogenolysis of the side chain with formation of complete and partial dealkylation products: benzene, toluene, and ethylbenzene. Proceeding simultaneously with hydrogenolysis are reactions of hydrogenation of the benzene ring, contraction of a six-membered ring to a five-membered, hydrogenolysis of the latter, and isomerization of the side chain of the original hydrocarbon (propyl into isopropyl, and vice versa).

4. The transformations of the investigated hydrocarbons included their methylation by methylene radicals formed by the decomposition of cycloalkanes (produced in the process) at the surface of the nickel-alumina catalyst.

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REACTIVITY AND MOLECULAR OPTICAL PROPERTIES OF ALKENYLSILANES

A. D. Petrov, Yu. P. Egorov, V. F. Mironov, G. I. Nikishin, and A. A. Bugorkova

There is much information in the literature on the evaluation of the effect of σ, π-conjugation on reactivity in various organic compounds [1]. In the case of organosilicon compounds the conjugation of double bonds with an Si—C bond has not yet been noted, and the reactivities of conjugated and nonconjugated double bonds in alkenylsilanes of various structure have not been subjected to a comparative quantitative study.

Over a period of years we have synthesized various unsaturated "silahydrocarbons" having a double bond in the α-, β-, γ-, or δ-position with respect to the silicon atom, and on several occasions we have pointed out qualitative differences between these alkenylsilanes in addition reactions [2-11]. We noted the exceptionally high activity of 2-alkenylsilanes (allylsilanes) in reactions with HBr, BR_2, $HS_2P(OR)_2$, and other substances [3-10]. For example, $(C_2H_5)_3SiCH_2CH=CH_2$ combined almost instantaneously with HBr at -70° [2], whereas $(C_2H_5)_3SiCH=CH_2$ [3], $(CH_3)_3SiCH_2CH=CH_2$ [4] and $(C_2H_5)_3SiCH_2CH_2CH=CH_2$ [5] reacted extremely slowly with HBr even at room temperature. Moreover, it was established that HBr adds to $(C_2H_5)_3SiCH=CH_2$ in the direction contrary to that by Markovnikov's rule [3], that it adds to $(C_2H_5)_3SiCH_2CH=CH_2$ entirely in the direction required by the rule [5] even in presence of peroxide [6], and that $(CH_3)_3SiCH_2CH_2CH=CH_2$, though undergoing addition of HBr in accordance with the rule, like the olefine [4], is also able to react contrary to the rule with HBr in presence of peroxides [12].

In the present investigation—with the object of evaluating quantitatively the effect of molecular structure on double-bond reactivity in alkenylsilanes, and with the object also of examining the phenomenon of alternation—we selected the thiocyanation reaction [13] (readily controllable with respect to time) and the intensities of the characteristic double-bond frequencies in the Raman and infrared spectra as objects for study. As can be seen from the results cited below, the alternation of the intensities of the Raman spectrum lines (double-bond frequencies 1630-1649 cm^{-1}) can be observed as far as the δ-position of the double-bond (Fig. 1). The intensity of these frequencies is least for the α-position, greatest for the β-position, and intermediate in value for the γ-position. An analogous curve is obtained for the variation of the intensity of the C = C band ($\sim$6.2 μ) in the infrared adsorption spectra (Fig. 2).

On the basis of refractometric measurements Fajans [14] concluded that the alternation of charges proceeds beyond the β-position. Whereas the alternation in the effect of the silicon atom on the direction of HBr addition ends at the β-double bond, the alternation in the rate of thiocyanogen addition extends to the γ-position (Fig. 3); beyond this there is a uniform diminution of the effect of the silicon atom along the carbon chain. It can be seen from the same graph that, in compounds of the type $R_3Si(CH_2)nCH=CH_2$ where $n = 0-4$, the double-bond is ten times (for the 5-minute and 1-hour curves) as active when $n = 1$ (2-alkenylsilanes) than when $n = 0$ (1-alkenylsilanes); 1-alkenylsilanes have about one-quarter of the activity of 3-alkenylsilanes ($n = 2$) and are approximately equal in activity to 4- and 5-alkenylsilanes.

The parallelism between the physical and chemical properties of alkenylsilanes of the type $R_3Si(CH_2)nCH=CH_2$ extends also to alkenylsilanes of other types. It was found that the presence of a methyl group at the double bond, irrespective of its position with respect to the Si atom, greatly raises the chemical activity of the double bond and the intensities of its characteristic frequencies in the Raman spectrum. For example, the intensities of the C = C frequencies of $(CH_3)_3SiC(CH_3)=CH_2$ and $(CH_3)_3SiCH=C(CH_3)_2$ were found to be 50 % greater than those of $(C_2H_5)_3SiCH=CH_2$. Still more marked was the continuous increase in the rate of thiocyanogen addition in a series of vinylsilanes, ranging from the unsubstituted vinyl compound, through the 2- and 1-methylvinyl compounds, to the 1,2-dimethylvinyl compound (Fig. 4).

For the 3-alkenylsilanes $(CH_3)_3SiCH_2CH_2CH=CH_2$ and $(CH_3)_3SiCH_2CH_2C(CH_3)=CH_2$ the rates of thiocyanation

differ greatly, the rate for the second compound being ten times as high as that for the first.

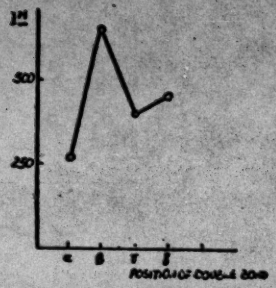

Fig. 1.

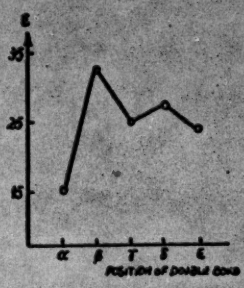

Fig. 2.

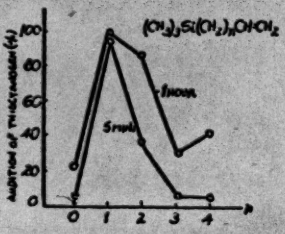

Fig. 3.

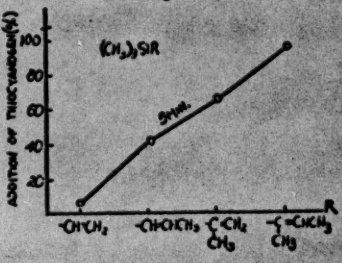

Fig. 4.

Comparison of calculated and determined molecular refractions for compounds of the type $R_3Si(CH_2)nCH=CH_2$ shows definite exaltation for allylsilanes ($n=1$), but absence of any exaltation in compounds for which $n=0,2,3$, and 4. For polyallylsilanes the exaltation rises in proportion to the number of allyl groups [15]. Alkenylsilanes having a branch at the double bond (for example, $(CH_3)_3SiCH=C(CH_3)-CH_3$, $(CH_3)_2SiCH_2CH_2C(CH_3)=CH_2$), irrespective of the position of the double bond with respect to the silicon atom, also show exaltation of molecular refraction [7, 11]. It is interesting to note that exaltation was found also when saturated ethyl and butyl radicals were attached to the silicon atom, but not in the case of methyl and propyl radicals (Table 1).

These phenomena were revealed when we calculated MR from the generally accepted values of the bond refractions [16] (Table 1). The use of group refractions for radicals attached to silicon as calculated by us from the constants of a large number of compounds has greater accuracy and convenience for the calculation of MR.

The peculiar physical properties of the allylsilanes, such as the high intensity of the double-bond Raman lines and infrared bands and the exaltation of molecular refraction, and also their high chemical activity, clearly indicate the presence in these compounds of conjugation between the double bond and the Si—C bond (σ, π-conjugation). Alkenylsilanes having methyl groups at the double bond also have these same physical and chemical peculiarities, and in this case the explanation lies in the conjugation of the double bond with C—H bonds of the CH_3 group, the hydrogens of which are strongly protonized.

An interesting peculiarity of the silicon atom is its "barrier" character with respect to the transmission of interaction between the radicals that are attached to it. This peculiarity is manifested in the proportionate growth of the intensity of the lines characterizing the $CH_2CH=CH_2$ group [15], in the constancy of the intensity of the C=C frequencies when the radicals attached to silicon are varied [17], in the stability of the characteristic frequencies in various saturated radicals [17,18], in the proportionate growth of the exaltation of molecular refraction with increase in the number of alkenyl groups, and in the nondependence of the rate of thiocyanogen addition on the number of alkenyl groups (Table 2) [13]. It may be supposed that this property is to be explained

both by the large mass of the silicon atom (as compared with carbon) and also by its greater atomic volume.

TABLE 1

Group Refractions of some Radicals attached to Silicon (ml/mole)

No.	Group attached to silicon	Our determined value of the refraction of Si—C bond	Group refraction	
			Found by us	Calculated [16]
1	Si—CH=CH$_2$	2.5	11.73	11.73
2	Si—CH$_2$CH=CH$_2$	2.68	16.54	16.36
3	Si—CH=CH—CH$_3$	2.85	16.71	16.36
4	Si—C(CH$_3$)=CH$_2$	2.5	16.36	16.36
5	Si—CH$_2$CH$_2$CH=CH$_2$	2.5	20.99	20.99
6	Si—CH$_2$C(CH$_3$)=CH$_2$	2.55	21.04	20.99
7	Si—CH=C(CH$_3$)—CH$_3$	2.95	21.44	20.99
8	SiCH$_2$CH$_2$C(CH$_3$)=CH$_2$	2.7	25.82	25.62
9	Si—C≡C—CH=CH$_2$		20.68	19.38
10	Si—CH$_3$	2.5	7.57	7.57
11	Si—C$_2$H$_5$	2.38	12.08	12.20
12	Si—n-C$_3$H$_7$	2.5	16.83	16.83
13	Si—n-C$_4$H$_9$	2.42	21.38	21.46
14	Si—CH$_2$Cl	2.5	12.41	12.41
15	Si—CH$_2$OH	2.5	9.12	9.12
16	Si—CH$_2$SCN	—	19.93	—
17	Si—Br	2.6	10.30	10.20
18	Si—OH	2.52	3.5	3.48

The rate of the thiocyanation reaction was determined by the method described earlier [13].

The Raman spectra were measured in the usual way [19]; the intensity was evaluated on the scale adopted in the USSR, on which the intensity of the 802 cm^{-1} line of cyclohexane is taken to be 250 units. In the comparison of the intensities of the Raman frequencies of C = C bonds in various alkenylsilanes, the integral value of the intensity was used; it was determined photometrically [19].

The infrared adsorption spectra were determined with an IKS-11 spectrometer by the usual method. In estimating the intensity of a band, we considered its value at the maximum and corrected it for the width of the slit [20]. Below we give the Raman spectra of the compounds discussed in this paper or prepared for the first time.

3-Butenyltriethylsilane $CH_2 = CHCH_2CH_2Si(C_2H_5)_3$ (I)

$\Delta\nu$: 168 (10) 267 (8b), 302 (10), 435 (6), 556 (60b), 617 (1), 636 (b) . 735 (3), 765 (7), 913 (12), 973(15), 1005 (20b),1020(20b), 1112 (10b), 1134(5), 1172 (2), 1197 (2), 1236 (20), 1279 (15), 1296 (20),1376(2),1414(40), 1468 (30), 1640 (50), 2879 (150b), 2902 (100b), 2938 (10), 2954 (55), 3000 (40), 3083 (20).

3-Butenylethyldimethylsilane $CH_2 = CHCH_2CH_2Si(CH_3)_2C_2H_5$ (II)

$\Delta\nu$: 153(15), 174 (15), 208 (10), 466 (6), 517 (10), 579 (60), 602 (5), 685 (15), 710 (10), 833 (5), 900 (10b), 913 (10b), 972 (2), 990 (2), 1015 (15), 1114 (5), 1164 (8), 1181 (8), 1234 (1), 1249 (8), 1280 (20), 1298 (20), 1359 (5),1416 (35), 1455 (10), 1640 (50), 2846 (8), 2878 (1000b), 2900 (100b) . 2940 (2), 2955 (60), 2972 (5), 3000 (45), 3080 (20).

3-Butenyltrimethylsilane $CH_2 = CHCH_2CH_2Si(CH_3)_3$ (III)

$\Delta\nu$: 148 (20), 207 (35 background), 247 (10 background), 274 (5), 324 (10), 438 (10) 518 (5b), 577 (10), 588 (30sh), 613(15sh), 685 (10), 802 (20), 850 (5), 889 (5), 899 (15b), 913 (15b), 990 (5), 1015 (12), 1115 (5) 1176 (5), 1252 (10), 1280 (20), 1298 (25), 1415 (10), 1445 (5), 1640 (60), 2845 (20), 2885 (100b), 2899 (150b), 2959 (80), 2972 (5), 3000 (20), 3080 (20).

TABLE 2

Rate of Addition of Thiocyanogen to Alkenylsilanes

Formula of Alkenylsilane	Amount of thiocyanogen added (%)		
	5minutes	1 hour	1 day
$(C_2H_5)_3SiCH=CH_2$	4.8	19.4	89.3
$(CH_3)_2SiCH=CHCH_3$	42.1	99	99.5
$(CH_3)_2SiC(CH_3)=CH_2$	64.3	80.7	98.9
$(CH_3)_2SiC(C_2H_5)=CH_2$	41.2	52.5	91.4
$(C_2H_5)_2SiCH=CCH_3$ $\quad\quad\quad

1176 (5), 1252 (10), 1280 (20) 1298 (25), 1415 (30), 1445 (5), 1640 (60), 2845 (10), 2880 (100b), 2899 (150b), 2959 (80), 2972 (5), 3000 (40), 3080 (20).

Trimethyl(2-methylpropenyl)silane $(CH_3)_3SiCH=C(CH_3)_2$ (IV)

$\Delta\nu$: 167 (20 background), 210 (20 background), 227 (30b), 252 (5), 363 (10), 452 (25), 615 (120), 662 (6), 690 (30b), 836 (8), 1061 (10), 1120 (5), 1148 (5), 1250 (10), 1310 (15), 1370 (25), 1414 (8), 1445 (40), 1623 (55) 2851 (30), 2905 (75b), 2930 (10sh), 2956 (85b).

Dimethyldi(2-methylpropenyl)silane $(CH_3)_2Si[CH=C(CH_3)_2]_2$ (V).

$\Delta\nu$: 169 (5 background), 224 (15b), 284 (15b), 306, 352 (15), 448 (6), 465 (12), 629 (2), 650 (20) 683 (15), 695 (5b), 830 (5), 849 (5), 1064 (15), 1120 (2), 1149 (4), 1251 (6), 1310 (20), 1372 (35), 1414 (3), 1444 (55), 1623 (70), 2856 (35), 2899 (20), 2908 (75b), 2927 (20), 2959 (25 doublet).

Trimethylpropenylsilane $CH_3CH=CHSi(CH_3)_3$ (VI)

$\Delta\nu$: 144 (10), 208 (40), 228 (30), 307 (25b), 336 (25), 390 (50), 508 (3), 615 (115), 684 (30), 705 (25b), 768 (7), 835 (12b), 1038 (5), 1110 (5), 1258 (15), 1315 (50), 1374 (15), 1415 (10), 1446 (25), 1621 (60), 2853 (20), 2898 (100), 2921 (50), 2967 (85b).

Isopropenyltrimethylsilane $CH_2=C(CH_3)Si(CH_3)_3$ (VII)

$\Delta\nu$: 148 (20b), 214 (30b), 242 (25), 290 (15), 370 (10), 570 (85), 652 (25), 690 (25), 757 (2), 835 (8), 938 (15), (1222), 1258 (10), 1372 (8), 1415 (50), 1444 (5), 1605 (55), 2856 (5), 2900 (80), 2965 (95), 3050 (15).

Trimethyl(2-methylallyl)silane $CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}CH_2Si(CH_3)_3$ (VIII)

$\Delta\nu$: 165 (40b), 235 (30), 267 (10), 391 (5), 423 (15), 490 (30sh), 597 (150), 658 (15), 690 (20), 716 (5), 769 (2), 828 (18), 871 (15), 974 (2), 998 (5), 1126 (25), 1160 (25), 1260 (5b), 1282 (7), 1315 (2), 1396 (15), 1410 (25), 1440 (5), 1638 (70), 2900 (100), 2912 (30) 2968 (80b), 2983 (20), 3080 (20).

2,2,5,5-Tetramethyl-2,5-disila-3-hexene $(CH_3)_3SiCH=CHSi(CH_3)_3$ (IX).

$\Delta\nu$: 183 (35b), 228 (15b), 325 (25), 610 (300), 683 (10), 698 (50), 789 (5), 842 (10), 882 (2), 1248 (15), 1258 (15), 1295 (40sh), 1387 (2), 1412 (20b), 1551-1571 (20 very b), 2900 (150), 2928 (25), 2961 (150).

In the spectra of compounds (I-III), which contain the group $CH_2=CHCH_2CH_2$– at Si, there is a group of stable frequencies 913, 1112, 1280, 1298, 1640, 3000, 3080 cm^{-1} which probably belong to vibrations in the terminal $CH=CH_2$ group. In the 2-methylpropenylsilanes (IV) and (V) the characteristic lines 1064, 1310, 1370, and 1623 cm^{-1} are present. The intensity of these lines increases with increase in the number of 2-methylpropenyl groups. We must point out the increase in the double bond frequency from 1594 cm^{-1} in vinylsilanes to 1623 cm^{-1} in 2-methylpropenylsilanes. A very similar value for the C=C frequency is found also in the compound (VI) (1621 cm^{-1}). Thus, the displacement of the double bond from the end to the second place in the chain causes an increase in its characteristic frequency by 30 cm^{-1}. – behavior that is generally observed also in alkenes. In compounds (VII) and (VIII) a CH_2 group is attached to the first carbon atom (reckoned from the direction of Si) of the C=C bond and this immediately causes a rise in the C=C frequency from 1594 and 1630 cm^{-1} to 1605 and 1638 cm^{-1}, respectively. The α-position of the $=CH_2$ group is also very well characterized by the position of the antisymmetrical frequency of C–H in this group (3050 cm^{-1}); in β-, γ-, and δ-positions it is always higher, being 3080 cm^{-1}. In the compound (IX) there is a broadening of the double-bond frequencies by 20 cm^{-1}, which may be explained by cis-trans isomerism and by the breadth of these lines.

SUMMARY

1. It was established that there is a parallelism between the rates of thiocyanogen addition and the intensity of Raman lines for a large number of alkenylsilanes of various structures.

2. It was shown that allylsilanes and alkenylsilanes having a tertiary double bond are characterized by particularly high double-bond activity in addition reactions, by high-intensity Raman lines and infrared absorption bands, and by exaltation of molecular refraction. It was suggested that these peculiarities of the above classes of alkenylsilanes are to be attributed to σ,π-conjugation.

3. It was shown that the alternation in the intensities of the double-bond lines of the Raman spectrum and absorption bands of the infrared spectra extends to the δ- and ϵ-double-bond positions, and the alternation in the rates of thiocyanogen addition extends to the γ-double-bond position.

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HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF ISOPROPYLBENZENE UNDER HIGH PRESSURES OF HYDROGEN

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The thermal decomposition of isopropylbenzene has been investigated by several authors. In a paper by Dobryansky, Kanep, and Katsman [1] data are given on the pyrolysis of isopropylbenzene at 650°. They obtained 88.7 % of liquid products and 9.1 % of gas. Among the liquid products they found benzene (6%), toluene (0.5%), and styrene (44%). Among the gaseous products they found H_2 (28.8%) and hydrocarbons: C_2 3.4%, C_3 6.8% C_nH_{n-2} 60.0% the amounts of methane and hydrogen being approximately equal. In another investigation a study was made of the thermal decomposition of isopropylbenzene occurring in the course of ten minutes at 586° under a pressure of 400 mm [2]. Analysis of the gaseous products of the reaction showed that it contained about 27% of hydrogen, about 60% of methane, and about 13% of ethane. In 1952 there appeared a study of the thermal cracking of isopropylbenzene in a flow apparatus at 700°, the time in the heating zone being 0.011second [3]. The total extent of the transformation of isopropylbenzene was (as a mole percentage) 2.1, the products including α-methylstyrene 1.3, styrene 0.4, xylenes 0.1, toluene 0.1, and benzene 0.21. Among the gaseous products were found (mole-%): hydrogen 1.6, methane 0.8, ethylene 0.1, and propene 0.1. Leigh and Szwarc [4] studied the pyrolysis of isopropylbenzene at 639-728° in a flow system in presence of a large excess of toluene, the time of contact being 0.41-0.46 second. They established that the primary act of the thermal decomposition of isopropylbenzene is the reaction:

$$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5\dot{C}HCH_3 + \dot{C}H_3$$

A paper appearing in 1953 [5] describes an investigation of the thermal transformation of isopropylbenzene in a flow system at 479°, 501°, and 528° (at space velocities if 1.00, 1.35, and 1.46 hr^{-1}, respectively) under a pressure of 816 atm. The total extents of conversion of the isopropylbenzene under these conditions were 22.6, 45.8, and 76.0%, respectively. Among the liquid reaction products a considerable amount of propylbenzene was found, the yield falling with rise in temperature (55.9 mole-% on the isopropylbenzene that reacted at 479°; 17.8 mole-% at 528°). At 479° no benzene could be detected among the reaction products and the yields of toluene and ethylbenzene (mole-% on the amount of isopropylbenzene that reacted) were 5.1 and 15.4, respectively; at 528° the yields were 5.1 of benzene, 26.5 of toluene, and 22.8 of ethylbenzene. At 479° the gaseous reaction products included (mole-%) 10.4 of hydrogen, 70.0 of methane, 9.2 of ethane, 5.4 of propene, 5.4 of propane, and 1.3 of the butane isomers. At the higher temperature of 528°, the contents (mole-%) of the gases were 0.6 of hydrogen, 77.8 of methane, 15.0 of ethane, 0.5 of propene, 5.0 of propane, and 1.0 of the butane isomers. These data show that, in the thermal decomposition of isopropylbenzene, a mixture containing a large number of hydrocarbons is formed; in addition to the thermal decomposition of isopropylbenzene there occurs the dehydrogenation of this substance and its decomposition products (into styrene and α-methylstyrene), and also the formation of propylbenzene.

Carrying out the thermal cracking of alkylbenzenes in presence of hydrogen (homogeneous destructive hydrogenation) has a substantial effect on the rate and direction of the decomposition processes, leading to the formation of mainly benzene. Some data on the homogeneous destructive hydrogenation of alkylbenzenes (toluene, ethylbenzene, propylbenzene, and butylbenzene) are given in the review article by Nemtsov [6]. The author considers that this process is a bimolecular reaction between the alkylbenzene and hydrogen. In this work it is shown that a metal packing has no effect on the reaction rate. In the reaction of ethylbenzene it was found that the yield of benzene increased and that of toluene diminished as the hydrogen pressure was increased. In a previous investigation [7] we studied the homogeneous destructive hydrogenation of toluene at 455-490° under hydrogen pressures of up to 1350 atm. On the basis of the results obtained we developed a scheme for the process based on a chain mechanism. In the present paper we give the results of an investigation on the homogeneous destructive hydrogenation of isopropylbenzene under high pressures of hydrogen.

EXPERIMENTAL

The investigation was carried out in a shaken stainless steel autoclave having a hydraulic seal (volume with manometer about 105 ml). Isopropylbenzene was introduced into the reactor, which was then closed. The pressure in the reactor was raised by means of a multiplying device fed from a cylinder. The isopropylbenzene was first distilled through a 30-plate column; it had the following constants: b.p. 152.2-152.4° (760 mm); n_D^{20} 1.4915. The literature [3] gives b.p. 152.39° (760 mm); n_D^{20} 1.4915. The charge of isopropylbenzene was the same in all experiments (30 g). In the various experiments the initial pressure of hydrogen ranged from 50 to 300 atm. The reactor was then heated to the required temperature.

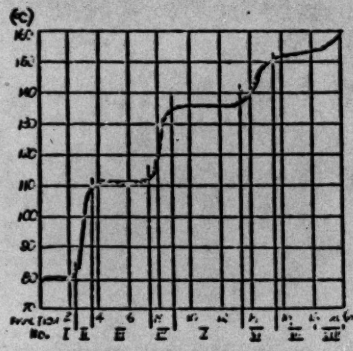

Fig. 1. Fractionation curve for liquid products of Experiment 19 (475°, P_{H_2} initially 50 atm, 5 hours)

The temperature was measured by means of a thermocouple contained in a long pocket inside the reactor which passed through the hydraulic seal. The temperature was maintained constant within ±2°. For this experiment the reactor was maintained at the required temperature for the required time and then cooled. In various experiments the working pressure ranged from 170 to 680 atm. At the end of the experiment the pressure was slowly lowered to that of the atmosphere. The liquid products were fractionated through a 30-plate column, fractions containing benzene, toluene, ethylbenzene, and isopropylbenzene being separated. A typical fractionation curve for liquid products obtained at an initial hydrogen pressure of 50 atm is given in Fig. 1. On this curve four horizontal portions – corresponding to benzene, toluene, ethylbenzene, and isopropylbenzene – can be clearly seen. In the fractions isolated, unsaturated hydrocarbons were estimated bromometrically; only very small amounts were found. Thus, for a working pressure of 190-210 atm, the bromine values of fractions boiling below 137° were only 0.1-0.5, and those of fractions boiling at 137-159°, 1.2-3.1. For the highest working pressures (680 atm) the corresponding fractions contained no unsaturated hydrocarbons at all. Hence, in calculating the benzene, toluene, ethylbenzene, and isopropylbenzene contents, we took no account of the presence of unsaturated hydrocarbons. In the fractionation we separated the following fractions:

Fraction I	b.p. up to 81°		Fraction V	b.p.	135–137°
Fraction II	b.p.	81–110°	Fraction VI	b.p	137–151°
Fraction III	b.p.	110–111°	Fraction VII	b.p.	151–153°
Fraction IV	b.p.	111–135°	Fraction VIII (in some cases up to 159°).	b.p.	153–156°

The residues were investigated separately.

The gaseous products were first investigated for their contents of hydrogen and unsaturated hydrocarbons by Hempel's method. They were then fractionated through a Podbielniak column, and the methane, ethane, and propane fractions were again investigated by Hempel's method. Fractionation curves for the gaseous hydrocarbon products from experiments at initial hydrogen pressures of 50 and 300 atm are given in Figures 2 and 3.

The contents of gaseous saturated hydrocarbons in the reaction products were calculated from the fractionation curves. Toward the end of the fractionation the temperature in the column began to rise (to −10°–0°) as a result of the exhaustion of the gas being fractionated. There were no plateaux on the curve corresponding to butane or isobutane, and we therefore took the fraction boiling above −65.3° to be propane. There were small amounts of ethylene in the ethane fraction, but no unsaturated hydrocarbons could be detected in the propane fraction.

RESULTS OF THE INVESTIGATION

a) Effect of the Hydrogen Pressure on the Content of Unsaturated Hydrocarbons in the Reaction Products. The effect of pressure on the content of unsaturated hydrocarbons in fractions boiling up to 156–159° is discussed above. The bromine values of the high-boiling products (residues) are given in Table 1.

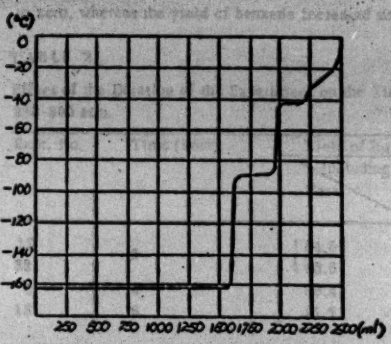

Fig. 2. Fractionation curve for gaseous products of Experiment 42 (475°, P_{H_2} initially 50 atm, 3 hours)

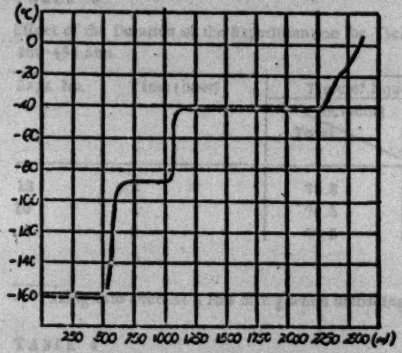

Fig. 3. Fractionation curve for gaseous products of Experiment 41 (475°, P_{H_2} initially 300 atm, 3 hours).

As will be seen from Table 1, the bromine numbers of the high-boiling products, which are 19.0-19.3 for a working pressure of 170-190 atm, are reduced to zero when the working pressure is 680-650 atm.

b) Effect of the Duration of the Experiment on the Rate and Direction of the Process. Data are given in Tables 2-4 on the effect of the duration of experiments at 475° on the composition of the liquid reaction products for a series of experiments carried out at a given working pressure.

It follows from Tables 2-4 that with increase in the duration of the experiment the yield of benzene increases at all pressures studied.

At a working pressure of 280-300 atm increase in the duration of the experiment from 3 to 6 hours results also in an increase in the yield of toluene. At a working pressure of 460-490 atm the yields of benzene are higher and those of toluene and ethylbenzene are lower than at a working pressure of 280-300 atm. Here again the yield of benzene increases with increase in the duration of the experiment, but the yields of toluene and ethylbenzene change very little. At a working pressure of 640-680 atm the yields of toluene and ethylbenzene are extremely small. The data in Tables 2-4 show also that the results of parallel experiments are in agreement; the average discrepancies in the yields of hydrocarbons are about 2% (on the charge).

c) Effect of Hydrogen Pressure on the Composition of the Liquid Reaction Products. In Tables 5-7 we give data relating to the effect of the pressure of hydrogen on the composition of the liquid reaction products for experiments differing in duration (3, 4, and 5 hours) at 475°.

TABLE 1

Quantity of Bromine Residue (b.p.>156°)

Expt. No.	Working pressure (atm)	Duration of Experiment (hours)	Bromine values
25	170-190	3	19.32; 19.04
19	190-210	5	12.51; 12.51
14	390	5	2.52; 2.51
13	490	2	1.63
7	490-480	5	1.38
4	660-650	5	0; 0

It follows from Tables 5-7 that, for a given time of reaction, with increase in hydrogen pressure the yields of toluene and ethylbenzene diminish and the yield of benzene and the amount of unchanged isopropylbenzene increase. For example, in three-hour experiments, with increase in pressure from 170-190 to 650-680 atm the yield of toluene and ethylbenzene is reduced by a factor of six, while that of benzene is increased by the same factor. The effect of pressure is seen equally clearly in the five-hour experiments. Increase in pressure from 190-210 to 640-660 atm resulted in falls in the yields of toluene and ethylbenzene from 15.6 and 19.5%, respectively.

to zero, whereas the yield of benzene increased six-fold.

TABLE 2

Effect of the Duration of the Experiment on the Yield of Reaction Product at 475° with a Working Pressure of 280-300 atm.

Expt. No.	Time (hour)	Yield of liquid products (% by weight on charge)*					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
12	3	84.5	22.0	7.8	14.7	26.4	10.8
38		85.5	19.7	6.5	14.1	29.9	12.9
8	4	85.4	22.6	10.6	17.3	18.4	13.2
15	6	81.7	23.7	11.4	15.8	15.7	12.6

* Taking into account a loss of 2 g when unloading reactor.

TABLE 3

Effect of the Duration of the Experiment on the Yield of Reaction Product at 475° with a Working Pressure of 460-490 atm.

Expt. No.	Time (hour)	Yield of liquid products (% by weight on charge)*					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
13	2	75.8	39.4	4.6	8.7	14.4	6.2
10	4	70.5	44.9	4.6	9.2	0	9.2
7	5	70.5	46.7	4.4	6.4	0	10.3

* Taking into account a loss of 2 g when unloading reactor.

TABLE 4

Effect of the Duration of the Experiment on the Yield of Reaction Product at 475° with a Working Pressure of 640-680 atm.

Expt. No.	Time (hour)	Yield of liquid products (% by weight on charge)*					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
33	2	75.3	41.3	2.2	5.0	17.9	5.3
34		75.2	43.4	2.8	5.2	13.6	7.2
35	3	67.6	46.3	1.7	1.8	10.1	5.3
36		71.8	47.9	1.8	2.8	10.3	6.2
41		69.1	49.0	2.2	4.6	5.2	5.5
27	4	66.3	50.9	2.8	1.8	0	8.6
4	5	68.8	55.9	0	0	0	9.8
28		66.0	53.3	0	0	0	10.6

* Taking into account a loss of 2 g when unloading reactor.

TABLE 5

Homogeneous Destructive Hydrogenation of Isopropylbenzene at 475° (in Three Hours)

Expt. No.	Working pressure (atm)	Yield of liquid products (% by weight on charge)*					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
25	170–190	90.1	8.1	11.3	19.0	31.2	18.7
12	290–300	84.5	22.0	7.8	14.7	26.4	10.8
38		85.5	19.7	6.5	14.1	29.9	12.9
17	370–400	78.2	35.9	4.0	10.5	20.7	4.3
37		76.5	36.0	4.5	9.7	19.6	4.8
35	650–680	67.6	46.3	1.7	1.8	10.1	5.3
36		71.8	47.9	1.8	2.8	10.3	6.2
41		69.1	49.0	2.2	4.6	5.2	5.5

* Taking into account a loss of 2 g when unloading reactor.

TABLE 6

Homogeneous Destructive Hydrogenation of Isopropylbenzene at 475° (in Four Hours)

Expt. No.	Working pressure (atm)	Yield of liquid products (% by weight on charge)*					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
8	290–280	85.4	22.6	10.6	17.3	18.4	13.2
10	480–460	70.5	44.9	4.6	9.2	0	9.9
27	660	66.3	50.9	2.8	1.8	0	8.6

* Taking into account a loss of 2 g when unloading reactor.

TABLE 7

Homogeneous Destructive Hydrogenation of Isopropylbenzene at 475° (in Five Hours)

Expt. No.	Working pressure (atm)	Yield of liquid products (% by weight on charge)*					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
19	190–210	81.6	9.2	15.6	19.5	14.7	19.5
14	390	75.4	37.4	4.2	10.1	12.2	7.1
7	480–490	70.5	46.7	4.4	6.4	0	10.3
4	640–660	68.5	55.9	0	0	0	9.8
28		66.0	53.3	0	0	0	10.6

* Taking into account a loss of 2 g when unloading reactor.

The fractionation curve for Experiment 4 is shown in Fig. 4. Comparison of this curve with the fractionation curve for the liquid product obtained at the same temperature and in the same time at a working pressure of 190–210 atm (Experiment 19, Fig. 1) clearly illustrates the effect of pressure on the direction of the process of homogeneous destructive hydrogenation of isopropylbenzene.

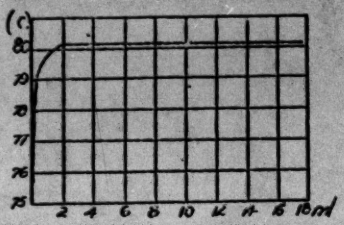

Fig. 4. Fractionation curve for liquid products of Experiment 4 (475°, P_{H_2} initially 300 atm, 5 hours)

As will be seen from the tables, the maximum yield of benzene was 55.9 % by weight on the amount of isopropylbenzene taken; the theoretical maximum yield is 65% by weight. We also carried out three- and five-hour experiments at 475° in absence of hydrogen. No benzene at all was obtained in these experiments; the yields of toluene and ethylbenzene were somewhat lower (respectively 6.0 and 12.8% in three hours, and 10.5 and 16.9% in five hours) than when hydrogen was present initially at 50 atm (Experiments 25 and 19). It must be concluded that the introduction of hydrogen into the sphere of reaction not only greatly accelerates the formation of benzene, but also accelerates the formation of ethylbenzene and toluene, although to a much lower extent.

Table 8 gives data on the effect of hydrogen pressure on the composition of the liquid products of reaction at 452° for five hours.

TABLE 8

Homogeneous Destructive Hydrogenation of Isopropylbenzene at 452° (in Five Hours)

Expt. No.	Working pressure (atm)	Yield of liquid products (% by weight on charge) •					
		Including / Total	Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
2	300–280	91.8	18.9	4.3	8.3	52.4	6.7
3	620–560	73.6	33.9	2.4	4.7	19.6	8.7

• Taking into account a loss of 2 g when unloading reactor.

It will be seen from Table 8 that at 452° increase of pressure from 300-280 to 620-560 atm resulted in a reduction (1.7 - and 1.8- fold, respectively) in the yields of toluene and ethylbenzene and a simultaneous increase (1.8 fold) in the yield of benzene; there was a 1.7-fold increase in the amount of unchanged isopropylbenzene.

d) Effect of Hydrogen Pressure on the Composition of the Gaseous Reaction Products. The results of the investigation of the gaseous reaction products are given in Table 9. The fractionation curves for the gaseous products of Experiments 41 and 42 are shown in Figures 2 and 3.

It will be seen from Table 9 and the fractionation curves that with increase in hydrogen pressure there is a considerable increase in the propane content of the gas with simultaneous reduction in the methane content. The variation with pressure of the ratio of the propane content to the sum of the methane and ethane contents is shown in Fig. 5, which indicates that this ratio is approximately proportional to the initial pressure of hydrogen.

e) Effect of Temperature on the Composition of the Liquid Reaction Products. Table 10 gives data on the effect of temperature on the yields of liquid reaction products for initial hydrogen pressures of 100 and 300 atm. It follows from Table 10 that at working pressures of 280-300 atm (initial hydrogen pressure 100 atm) a lowering of the temperature from 475° to 452° results in a 2.5-fold reduction in the yield of toluene and a two -fold reduction in the yield of ethylbenzene. The yield of benzene is very slightly reduced (by 4-5 %). The proportion of unchanged isopropylbenzene is reduced from 83.0 to 47.6%, which indicates a high temperature coefficient for the reaction.

TABLE 9

Analysis of Gaseous Reaction Products (3-hour experiment)

Expt. No.	Pressure (atm)		Contents of all gases, including H_2, (%)					Content of gases (% on gases other than H_2)			
	H_2, initial	working	H_2			C_3H_6	C_2H_4	CH_4	C_2H_6	C_3H_8	C_4H_8
42	50	190–210	29.4	45.5	10.1	14.6	0.38	64.5	14.2	20.8	0.53
38	100	300–290	44.8	29.6	6.3	18.9	0.36	53.7	11.5	34.15	0.65
37	150	400–370	48.4	17.1	11.7	22.5	0.30	33.2	22.6	43.6	0.60
41	300	680–650	62.2	8.0	7.4	22.3	0.05	21.2	19.6	59.1	0.14

TABLE 10

Effect of Temperature on the Yields of Liquid Reaction Products

Expt. No.	Time (hours)	Temperature (°C)	Working pressure (atm)	Liquid products (% by weight on charge)*					
				Total	including Benzene	Toluene	Ethylbenzene	Isopropylbenzene	Fraction boiling above 156°
2	5	452	300–280	91.8	18.9	4.3	8.3	52.4	6.7
8	4	475	290–280	85.4	22.6	10.6	17.3	18.4	13.2
15	6	475	300	81.7	23.7	11.4	15.8	15.7	12.6
3	5	452	620	73.6	33.9	2.4	4.7	19.6	8.7
4	5	475		68.5	55.9	0	0	0	9.8
28	5	475	640–660	66.0	53.3	0	0	0	10.6

* Taking into account a loss of 2 g when unloading reactor.

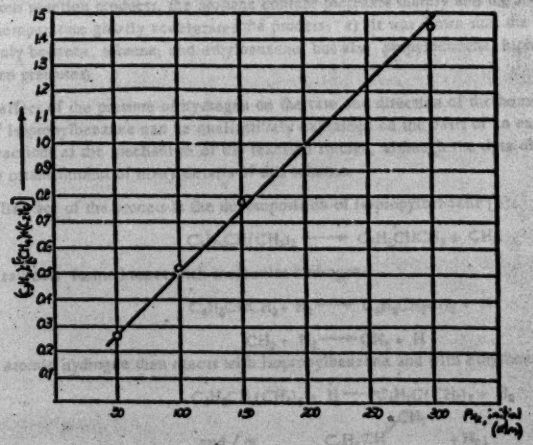

Fig. 5. Effect of the Initial Hydrogen Pressure on the Ratio, $(C_3H_6):[CH_4+(C_2H_6)]$ at 475° (3 hours).

f) Investigation of the High-boiling Reaction Products. As it could be expected that under the conditions of our experiments propylbenzene would be formed [5], we attempted to isolate propylbenzene from the high-boiling reaction products (residues, b.p. above 156°). Fractionation of these residues yielded propylbenzene, b.p. 158.7-159.2° (760 mm); n_D^{20} 1.4920 (the literature gives b.p. 159.22°; n_D^{18} 1.4920). Propylbenzene was acetylated by the method described in the paper [9]; the semicarbazone obtained from the propylacetophenone melted at 181.0-181.5° (the literature [5] gives 181.0-181.5°). Analysis of the semicarbazone gave:

Found%: N 19.32

$C_{12}H_{17}N_3O$. Calculated%: N 19.13

From the high-boiling residues obtained in experiments at an initial hydrogen pressure of 300 atm, biphenyl was isolated. It melted at 69.5-70° (the literature gives 70.0°), and there was no melting point depression in admixture with pure biphenyl.

Found%: C 93.29; 93.44; H 6.45; 6.59

$C_{12}H_{10}$. Calculated%: C 93.46; H 6.54

From the high-boiling residues obtained in experiments at an initial hydrogen pressure of 50 atm, naphthalene, m.p. 79.5-80°, was isolated.

Found%: C 93.37; 93.74; H 6.29; 6.31

$C_{10}H_8$. Calculated%: C 93.71; H 6.29

Fractionation of these residues yielded also a fraction having b.p. 277-280° (760 mm); n_D^{20} 1.5928. This fraction was evidently bitolyl [7].

Found%: C 92.35; 92.41 H 7.59; 7.56

$C_{14}H_{14}$. Calculated%: C 92.26; H 7.74

DISCUSSION OF RESULTS

The principal results of the investigation can be stated as follows: a) as would be expected, increase of the pressure of hydrogen in the homogeneous destructive hydrogenation of isopropylbenzene causes a decrease in the content of unsaturated hydrocarbons in the reaction products; b) increase of the pressure of hydrogen causes an increase in the overall rate of transformation of isopropylbenzene; c) increase of the pressure of hydrogen causes an increase in the yield of benzene and decreases in the yields of toluene and ethylbenzene; in the gaseous reaction products, the propane content increases sharply and the methane content diminishes; d) rise of temperature greatly accelerates the process; e) it was shown that the liquid reaction products include not only benzene, toluene, and ethylbenzene, but also propylbenzene, biphenyl, and naphthalene (at low hydrogen pressures).

The effect of the pressure of hydrogen on the rate and direction of the homogeneous destructive hydrogenation of isopropylbenzene can be qualitatively explained on the basis of an examination of a general scheme of chain reactions as the mechanism of the reaction studied, although the data obtained are of course insufficient for the establishment of many details of this scheme.

The first act of the process is the decomposition of isopropylbenzene [4]:

$$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5\dot{C}HCH_3 + \dot{C}H_3 \qquad (1)$$

The radicals formed react with molecular hydrogen:

$$C_6H_5\dot{C}HCH_3 + H_2 \longrightarrow C_6H_5CH_2CH_3 + \dot{H} \qquad (2)$$

$$\dot{C}H_3 + H_2 \longrightarrow CH_4 + \dot{H} \qquad (3)$$

The atomic hydrogen then reacts with isopropylbenzene and with ethylbenzene:

$$C_6H_5CH(CH_3)_2 + \dot{H} \longrightarrow C_6H_5\dot{C}(CH_3)_2 + H_2 \qquad (4)$$

and / or $C_6H_5CH(CH_3)(\dot{C}H_2) + H_2$;

$$C_6H_5CH(CH_3)_2 + \dot{H} \longrightarrow \dot{C}_6H_5 + C_3H_8 \qquad (5')$$

and / or $C_6H_6 + \dot{C}_3H_7$; $(5'')$

$\dot{C}_6H_5 + H_2 \longrightarrow C_6H_6 + \dot{H}$ (6). $\dot{C}_3H_7 + H_2 \longrightarrow C_3H_8 + \dot{H}$ (7)

$$C_6H_5C_2H_5 + \dot{H} \longrightarrow C_6H_5\dot{C}HCH_3 + H_2 \qquad (8)$$

and / or $C_6H_5CH_2\dot{C}H_2 + H_2$

$$C_6H_5C_2H_5 + \dot{H} \longrightarrow \dot{C}_6H_5 + C_2H_6 \qquad (9')$$

and / or $C_6H_6 + \dot{C}_2H_5$. $(9'')$

$$\dot{C}_2H_5 + H_2 \longrightarrow C_2H_6 + \dot{H}. \qquad (10)$$

Reactions (4) and (8) are suppressed by increase in hydrogen pressure. The ethylbenzene formed not only reacts with hydrogen by reaction (9), but also decomposes with formation of toluene:

$$C_6H_5\dot{C}HCH_3 \longrightarrow C_6H_5\dot{C}H_2 + \dot{C}H_3. \quad (11)$$

$$C_6H_5\dot{C}H_2 + H_2 \longrightarrow C_6H_5CH_3 + \dot{H}. \quad (12)$$

The homogeneous destructive hydrogenation of toluene has been examined by us previously [7].

The equations given above characterize essentially only the participation of hydrogen in the process under consideration. The complete scheme of the chain mechanism includes also the interaction among themselves of all of the radicals formed (recombination reactions and their interactions with all of the substances in the reaction sphere. An examination of the above equations shows that increase of hydrogen pressure will lead to increase in the concentration of atomic hydrogen; the interaction of the atomic hydrogen with isopropylbenzene molecules (and also with ethylbenzene and toluene) will therefore be accelerated with increase in the yield of benzene and acceleration of the overall transformation of isopropylbenzene. For the same reason the yield of propane will also be increased.

We remarked above that in our experiments at low initial hydrogen pressure there was some increase in the yields of ethylbenzene and toluene as compared with experiments in which hydrogen was absent. It is possible that this is to be explained by the occurrence of the following reactions [10]:

$$C_6H_5C_2H_5 + \dot{H} \longrightarrow C_6H_5\dot{C}H_2 + CH_4 \quad (13')$$

$$\text{or } C_6H_5CH_3 + \dot{C}H_3 \quad (13'')$$

and correspondingly

$$C_6H_5CH(CH_3)_2 + \dot{H} \longrightarrow C_6H_5\dot{C}_2H_4 + CH_4 \quad (14')$$

$$\text{or } C_6H_5C_2H_5 + \dot{C}H_3 \quad (14'')$$

but this matter requires further investigation.

SUMMARY

1. The homogeneous destructive hydrogenation of isopropylbenzene high pressures of hydrogen was investigated.

2. It was shown that increase in the pressure of hydrogen accelerates the transformation of isopropylbenzene, greatly increases the yield of benzene, reduces the yields of toluene and ethylbenzene, and brings about an increase in the propane content of the gaseous reaction products.

3. An explanation is advanced for the observed effects of the pressure of hydrogen on the rate and direction of the homogeneous destructive hydrogenation of isopropylbenzene.

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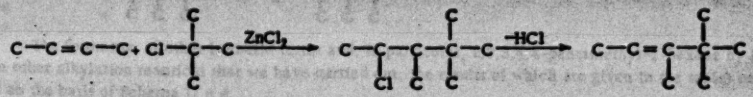
LOW-TEMPERATURE ALKYLATION OF α- AND β-OLEFINS WITH TERTIARY ALKYL HALIDES IN PRESENCE OF ZINC CHLORIDE

A. P. Meshcheryakov, E. I. Erzyutova, and A. D. Petrov

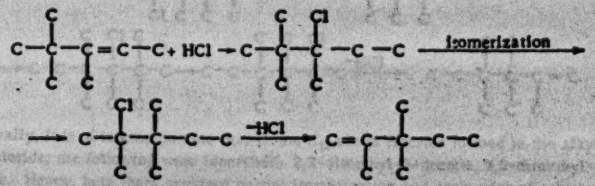
The reaction of catalytic alkylation of olefins with alkyl halides was discovered in 1878 simultaneously by Eltekov [1] and by Lermontova [2], who worked in Butlerov's laboratory. Only in the last decade has the use of this reaction been developed by Russian and foreign investigators, who have used it (and also the copolymerization reaction of 2-methylpropene and 2-butene) mainly for the synthesis of 2,2,3-trimethylbutane.

Our object in the present investigation was the further study of this reaction and the application of it to the preparation of alkylation products containing branched olefins ranging from C_8 to C_{16} and containing tertiary and quaternary carbon atoms. We studied the alkylation of 2-butene, 2-methyl-2-butene, 1-hexene, and 1-octene with tert-butyl chloride, 2-chloro-2,3-dimethylbutane, 2-chloro-2,3,3-trimethylbutane, and 4-chloro-4-propylheptane.

The investigation of the first of these reactions — the alkylation of 2-butene with tert-butyl chloride — already showed that, in spite of the low alkylation temperature (room temperature), there occurred not only the addition reaction — already noted by Lvov [3] and by Kondakov [4] and resulting in the formation of 3,4,4-trimethyl-2-pentene (25 % yield) — but also the formation by isomeric change of 2,3,3-trimethyl-1-pentene (26%) and 2,3,4-trimethyl-2-pentene (46%).

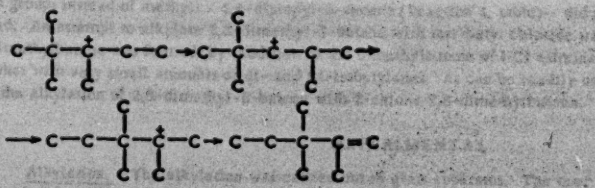


The formation of the first of these hydrocarbons can be described by reactions of addition and elimination of HCl in accordance with the rules of Markovnikov [5], Vagner [6], and Zaitsev [7] — reactions that are related to the replacement of chlorine by a methyl group as noted by Vagner [8], Favorsky [9], and Brown and Fletcher [10, 11].



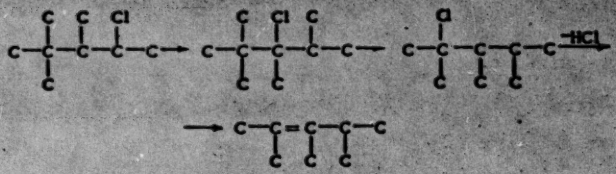
(Scheme 1)

The same reaction can be represented as addition of H^+ followed by reaction of the resulting ions [12]:

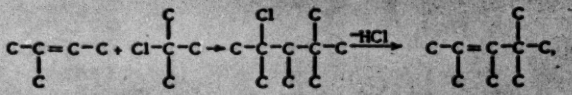


(Scheme 2)

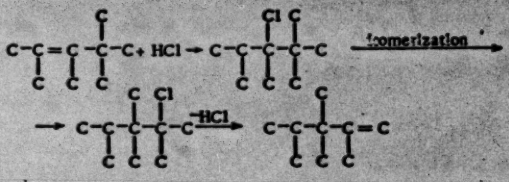
However, we prefer Scheme 1, by means of which we explain all of the reactions that we have studied. The formation of 2,3,4-trimethylpentene is represented as follows:



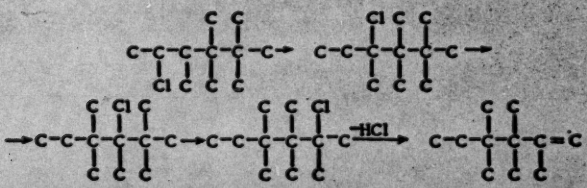
From the C_9 olefins obtained by the alkylation of 2-methyl-2-butene with tert-butyl chloride, in addition to the main product 2,3,4,4-tetramethyl-2-pentene, formed by the reaction



we isolated also 2,3,3,4-tetramethyl-1-pentene. The formation of this compound can be readily represented on the basis of Scheme 1, i.e. by the reaction:



The formation of other isomeric forms and, in particular, 2,3,3,4,4-pentamethyl-1-hexane by Reaction 3 (see the other alkylation reactions that we have carried out, the results of which are given in the table) can be represented on the basis of Scheme 1, e.g.



Finally, it is of interest to note that in the C_{12} olefin fraction formed in the alkylation of 1-octene with tert-butyl chloride, the following were identified: 2,2-dimethyl-3-decene, 2,2-dimethyl-4-decene, and 2,3-dimethyl-3-decene. Hence, here there occurred partial isomerization and conversion of a hydrocarbon with a quaternary carbon into one with two tertiary carbons. On the other hand, a hydrocarbon with a tertiary carbon in which there were propyl groups instead of methyls - 4,4-dipropyl-5-decene (Reaction 4, table)-- did not undergo isomerization of this kind. An attempt to alkylate 2,3-dimethyl-2-butene with tert-butyl chloride was not successful; only 2-chloro-2,3--dimethylbutane was formed (by addition to the dimethylbutene of HCl eliminated from tert-butyl chloride) together with very small amounts of di- and tri-isobutylenes. As can be readily understood, we did not succeed also in the alkylation of 2,3-dimethyl-2-butene with 2-chloro-2,3-dimethylbutane.

EXPERIMENTAL

Alkylation. The alkylation was carried out in glass apparatus. The reaction mixture consisted of olefin and alkyl halide (equivalent amounts) together with $ZnCl_2$ (10% on the weight of olefin taken). The reaction mixture was shaken for 6-8 hours each day at room temperature over a period of 10-12 days. The alkylation product was then decanted from zinc chloride, washed with a saturated solution of potassium carbonate, dried with calcium chloride, and fractionated. In the first fractionation unchanged olefin and alkyl halide were separated; the amount recovered unchanged was about 50% in all of the syntheses. The remaining mixture of alkyl halides and olefins formed in the reaction was then treated with hot caustic potash solution and was fractionated several times through an 18-

plate column. About thirty experiments were carried out on the alkylation of 2-butene with tert-butyl chloride, and 500 g of a C_8 olefin fraction was obtained, b.p. 108-116°, the yield being 35-39% (calculated on the basis of the amounts of 2-butene and tert-butyl chloride that reacted).

The fraction had b.p. 108-116°, d_4^{20} 0.7367; and n_D^{20} 1.4225

	Found %:	C 85.69; H 14.32
C_8H_{16}.	Calculated%:	C 85.63; H 14.37

Ozonization. Ozonized oxygen (about 6% ozone) was passed for 14 hours at 4 liters per hour through a solution of 10 g of C_8 olefins in 30 ml of chloroform. Altogether, 50 g of C_8 olefins was ozonized in portions. The ozonides were hydrolyzed with water and 10% hydrogen peroxide. The following ozonization products were isolated: 1) Acetone, identified a) as the semicarbazone, m.p. 183-184° and b) as the 2,4-dinitrophenylhydrazone, m.p.124.5° (a mixture test gave 124-125°; the literature [13] gives 126°). 2) 3 methyl-2-butanone, identified as its semicarbazone, m.p. 110-111.5° (a mixture test gave 110-111.5°; the literature [13] gives 113°). 3) Pinacolone, identified as its semicarbazone, m.p. 152-153° (a mixture test gave 153-154°; the literature [13] gives 157°). 4) 3,3--Dimethyl-2-pentanone, identified as its semicarbazone, m.p. 138-139° (the literature [14] gives 136-138°). In order to provide a sample for a mixture melting test, the ketone was synthesized from 1,1-dimethylpropylmagnesium chloride and acetyl chloride; the melting point of the semicarbazone of this ketone was 139-140°, and the melting point of the mixture was also 139-140°.

Analysis of the semicarbazone prepared from 3,3-dimethyl-2-pentanone:

	Found %:	N 23.76
$C_8H_{17}ON_3$.	Calculated%:	N 24.5

Acid ozonization products isolated were: formic acid (identified by the calomel method) and acetic acid (identified by the silver salt):

	Found %.	Ag 64.11
$C_2H_3O_2Ag$.	Calculated%:	Ag 64.63
	Found	M 59 (titration)
$C_2H_4O_2$.	Calculated	M 60

The C_8 olefin fraction (400 g) was hydrogenated in an autoclave over Bag's nickel catalyst; 100 g of the product was analyzed by the Raman spectrum method, and 300 g was demethylated, fractionated, and then analyzed spectrographically. The results confirmed the conclusions about the structures of the C_8 olefins which we had reached on the basis of the ozonization results.

The C_8 olefin fraction obtained by the alkylation of 2-methyl-2-butene with tert-butyl chloride had b.p. 128-134°, d_4^{20} 0.7550; n_D^{20} 1.4293.

	Found %:	C 85.61; H 14.45
C_8H_{16}.	Calculated%:	C 85.63; H 14.37

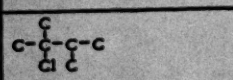
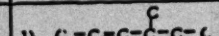
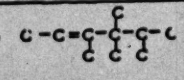
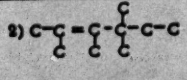
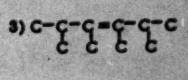
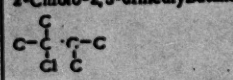
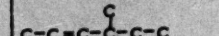
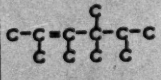
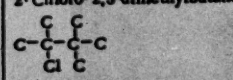
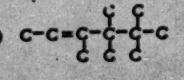
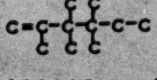
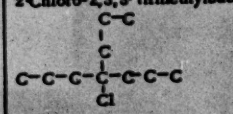
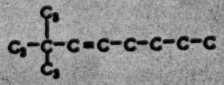
Ozonization of the C_8 olefins was carried out under the conditions indicated above. Formic acid was identified in the acid fraction, and acetone and pinacolone in the neutral fraction. Also, in the higher fraction of the oxidation products, b.p. 150-157°, 3,3,4-trimethyl-2-pentanone was identified (as semicarbazone, m.p. 147-148°; the literature [15] has 146.5-148.5°). In order to provide material for a mixture melting test, 3,3,4-trimethyl-2--pentanone was synthesized by hydrogenation over platinum of 3,3,4-trimethyl-4-penten-2-one, obtained by Kondakov's method from 2,3-dimethyl-2-butene and acetyl chloride in presence of zinc chloride. The semicarbazone of the 3,3,4-trimethyl-2-pentanone synthesized in this way melted at 148-149°.

	Found%:	N 22.45
$C_8H_{19}ON_3$.	Calculated%:	N 22.66

A mixture test on the semicarbazones of the ketone synthesized by us and the ketone obtained by ozonization of the C_8 olefins showed a melting point of 147.5-149°.

In the analysis of the ozonization products of the C_{12} fraction obtained by the alkylation of 1-octene by tert--butyl chloride, the only substance identified (by the method indicated above) in the neutral fraction was 3-methyl--2-butanone. By fractional precipitation of the acids as silver salts we isolated a C_7 acid (heptanoic), a C_8 acid

TABLE

Reaction No.	Tertiary alkyl halide	Olefin	Isolated alkylation products		
1			1) 	2) 	3) 
	2-Chloro-2,3-dimethylbutane	2-Butene	3,4,4,5-Tetramethyl-2-hexene	2,3,4,4-Tetramethyl-2-hexene	2,3,4,5-Tetramethyl-3-hexene
2				—	—
	2-Chloro-2,3-dimethylbutane	2-Methyl-2-butene	2,3,4,4,5-Pentamethyl-2-hexene	—	—
3			1) 	2) 	
	2-Chloro-2,3,3-trimethylbutane	2-Butene	3,4,4,5,5-Pentamethyl-2-hexene	2,3,3,4,4-Pentamethyl-1-hexene	
4				—	
	4-Chloro-4-propylheptane	1-Hexene	4,4-Dipropyl-5-decene		

(probably a mixture of hexanoic and 3,3-dimethylbutyric acids), and a C_5 acid (pivalic acid).

	Found%:	Ag 45.91
$C_7H_{13}O_2Ag$.	Calculated%:	Ag 45.51
	Found%:	Ag 47.79
$C_6H_{11}O_2Ag$.	Calculated%:	Ag 48.38
	Found%:	Ag 51.7
$C_5H_9O_2Ag$.	Calculated%:	Ag 51.61

The heptanoic acid was also converted into its amide, m.p. 91.5-92.5° (the literature give 96° [16]).

In the subsequent alkylation experiments (Reactions 1-3, table), in the analysis of the C_{10} and C_{12} olefin fractions we met the problem of identifying the same ketones (and also formic and acetic acids) as in the experiments described above. We shall therefore omit descriptions of the experiments and confine ourselves to the alkylation results obtained, which are given in the table. These results show that in the first reaction two additional isomeric hydrocarbons are obtained, in the second reaction there were none, and in the third reaction there was one. The first of the isomeric C_{10} olefins obtained in Reaction 1, 2,3,4,4-tetramethyl-2-hexene, is a form whose formation could be predicted from the laws of Scheme 1, i.e. successive addition and elimination of HCl and replacement of chlorine by methyl. The formation of the third C_{10} olefin, 2,3,4,5-tetramethyl-3-hexene, could not have been predicted, but its formation is readily explained by Scheme 2 as the result of the addition of H^+ to 2,3,4,4-tetramethyl--2-hexene and subsequent isomerization of a tertiary amyl group into a secondary amyl group. The absence of an isomeric form in Reaction 2 under the low-temperature conditions of alkylation studied and the formation of only one isomeric hydrocarbon in Reaction 3 are probably to be explained by reduced possibilities of isomerization arising from steric difficulties.

In conclusion, we will consider the C_{16} olefin fraction obtained by the alkylation of 1-hexene with 4-chloro--4-propylheptane (Reaction 4, table); b.p. 93-97° (2 mm), d_4^{20} 0.8137; n_D^{20} 1.4480. In the ozonization of this fraction no neutral products were found. Acid products isolated were: a liquid acid, b.p. 175-180°, and a crystalline acid. The latter was filtered off, and the silver salt of the liquid acid was prepared.

	Found%:	Ag 51.41
$C_5H_9O_2Ag$.	Calculated%:	Ag 51.61

Analysis of the crystalline acid (2,2-dipropylvaleric acid):

	Found M 183 (titration)	
$C_{11}H_{22}O_2$.	Calculated M 186	
	Found%:	Ag 36.00
$C_{11}H_{21}O_2Ag$.	Calculated%:	Ag 36.22

The crystalline acid was converted into its amide: 0.35 g of the acid and 5 ml of thionyl chloride were refluxed together for 30 minutes, and the mixture was then poured into 15 ml of concentrated ammonia cooled in ice. The precipitate was filtered off and recrystallized from dilute alcohol. It melted at 58-59° (for 2,2-dipropylvaleramide the literature [17] gives m.p. 69-70°).

4,4-Dipropyl-5-decene (8.5 g) was hydrogenated in pentane solution over nickel at 180-200° and an initial pressure of 80 atm. The product was 4,4-dipropyldecane, b.p. 119-121° (15 mm), d_4^{20} 0.7951; n_D^{20} 1.4398, (the literature [18] gives b.p. 124-126° (16 mm), d_4^{20} 0.7879; n_D^{20} 1.4398).

SUMMARY

1. A study was made of low-temperature alkylation of olefins with tertiary alkyl halides in presence of zinc chloride, and the relationship between the structure of the reactants and the character of the side reactions — isomeric changes accompanying the reaction of addition of chloroalkanes to alkenes — was elucidated.

2. It was established that in the alkylation of 2-butene, both with tert-butyl chloride and with 2-chloro-2,3--dimethylbutane, the octene and decene isomers predicted by theory are formed.

3. In the alkylation of 2-methyl-2-butene with tert-butyl chloride, only one isomeric form of the expected structure is formed (2,3,3,4-tetramethyl-4-heptene), and in alkylation with 2-chloro-2,3,3-trimethylbutane, again only one isomeric form is formed (2,3,3,4,4-pentamethyl-1-hexene).

4. In the alkylation of 2-methyl-2-butene with 2-chloro-2,3-dimethylbutane, only the addition reaction occurs, leading to the formation of 2,3,4,4,5-pentamethyl-2-hexene with absence of isomeric change.

5. It was shown that, whereas in the alkylation of 1-octene with tert-butyl chloride both 2,2-dimethyl-3-decene and 2,3-dimethyl-3-decene are formed (i.e. partial isomerization of a hydrocarbon with a quaternary carbon atom occurs), in the alkylation of 1-hexene with 4-chloro-4-propylheptane only 4,4-dipropyl-5-decene is obtained (i.e. a hydrocarbon with a quaternary carbon atom in which propyl groups replace methyl groups no longers undergoes isomerization).

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POLYORGANOALUMINOSILOXANES

K. A. Andrianov and T. N. Ganina

The first information on polyorganometallosiloxanes appeared in 1947. It was observed that organosilicon compounds containing hydroxyl groups form polymeric compounds with multivalent metals and their hydroxides, and it was shown that the chains of the polymers contain metallosiloxane groups [1]. The following scheme of reaction was proposed for the formation of polyorganoaluminosiloxanes:

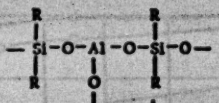
$$6HOSiR_2 \cdot OSiR_2OH + 2Al \rightarrow 2(HOSiR_2OSiR_2O)_3Al + 3H_2 \qquad (1)$$

It was later found [2] that triethylsilanol reacts with aluminum with formation of nonaethylaluminoxytrisiloxane [author's nomenclature] in accordance with the scheme:

$$6(C_2H_5)_3SiOH + 2Al \rightarrow 2[(C_2H_5)_3SiO]_3Al + 3H_2 \qquad (2)$$

Further investigations showed that polyorganometallosiloxanes can be prepared by the cohydrolysis of alkyl (or aryl) halosilanes and salts of multivalent metals and by metathetical reactions between hydrolysis products of organosilicon monomers and salts of multivalent metals.

As will be seen from Equation 1, polyorganoaluminosiloxanes consist of molecules having chains of the following structure:



They contain $-\overset{|}{\underset{|}{Si}}-O-$ and $-\overset{|}{\underset{|}{Si}}-O-Al-$ linkages.

It has been established by the study of various organosilicon compounds that the $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ linkage is capable of undergoing scission under the action of acid agents. For example, the $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ linkage of hexamethyldisiloxane is broken by the action of 20% oleum or a mixture of sulfuric acid and ammonium chloride or fluoride [3]. The available data on the action of acid reagents on the $-\overset{|}{\underset{|}{Si}}-O-Al-$ linkage indicate that, even in such complex compounds as aluminosilicates, this linkage undergoes scission under the action of hydrochloric and other acids. In polyorganoaluminosiloxanes the $-\overset{|}{\underset{|}{Si}}-O-Al-$ linkage differs considerably from that found in aluminosilicates, the oxygen being bound to silicon atoms carrying two or three organic radicals. This circumstance must naturally affect the stability of the $-\overset{|}{\underset{|}{Si}}-O-Al-$ linkage to acid scission. The organic radicals (CH_3, C_2H_5, C_6H_5) replacing the oxygen bonds of silicon in polyorganoaluminosiloxanes weaken the electrophilic character of silicon, which must lead to a strengthening of the electrophilic character of the aluminum atom in the $-\overset{|}{\underset{|}{Si}}-O-Al-$ linkage and therefore to an increase in the tendency of this linkage to undergo scission under the action of acid.

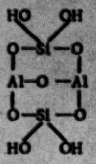
It is therefore of great interest to prepare polyorganoaluminosiloxanes and subject them to a scission reaction with the object of studying the stability of their $-\overset{|}{\underset{|}{Si}}-O-Al-$ linkages – as compared with those of aluminosilicates – to the action of aqueous hydrochloric acid. For this purpose we synthesized a polymer containing aluminum chemically bound to silicon atoms through oxygen, namely, polyaluminoxytetra(dimethylphenyldisiloxane) [author's nomenclature]. The synthesis was effected by the cohydrolysis of dichlorodimethylsilane, trichlorophenylsilane, and aluminum chloride in an alkaline medium:

$$R_2SiCl_2 + R'SiCl_3 + AlCl_3 \xrightarrow[NaOH]{H_2O} [OR_2SiOSiR']_4-O-\overset{|}{\underset{|}{Al}}-O-$$

We also synthesized the monomeric compound, nonaethylaluminoxytrisiloxane by dissolving aluminum in triethylsilanol:

$$6(C_6H_5)_2SiOH + 2Al \rightarrow 2[(C_6H_5)_2SiO]_3Al + 3H_2.$$

Our investigation of the scission of $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkages in polyaluminoxytetra(dimethylphenyldisiloxane) and nonaethylaluminoxytrisiloxane by means of hydrochloric acid was carried out in conjunction with comparative measurements on the natural mineral kaolin, which, according to Vernadsky [4], has the following formula:



It is known from the literature [5] that treatment of kaolin with 10 % hydrochloric acid in a boiling water bath for ten hours results in the rupture of

$-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkages.

In our experiments the scission of the

$-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkage in nonaethylaluminoxytrisiloxane, polyaluminoxytetra (dimethylphenyldisiloxane), and kaolin was effected with hydrochloric acid (10%, 20%, and 30%) at 96°. The experimental results, which are given in Fig. 1, show that in a one hour treatment with 10% hydrochloric acid the $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkages in polyaluminoxytetra(dimethylphenyldisiloxane) are ruptured to the extent of 79%, and those in kaolin to the extent of 90.8%. After five hours the respective figures are 65, 90.5, and 100%, after ten hours the extent of scission is 70% for polyaluminoxytetra(dimethylphenyldisiloxane) and 91% for nonaethylaluminoxytrisiloxane, and after 22 hours the $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkages in polyaluminoxytetra(dimethylphenyldisiloxane) are ruptured only to the extent of 79%.

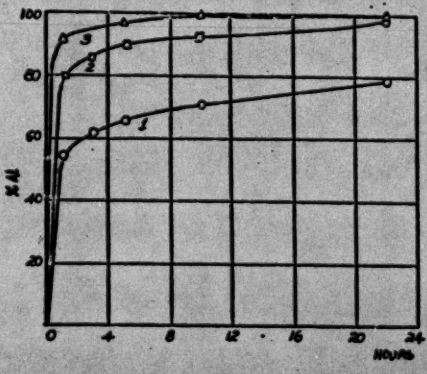


Fig. 1. Scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkage with 10% hydrochloric acid: 1 - polyaluminoxytetra(dimethylphenyldisiloxane) 2 - nonaethylaluminoxytrisiloxane; 3 - kaolin

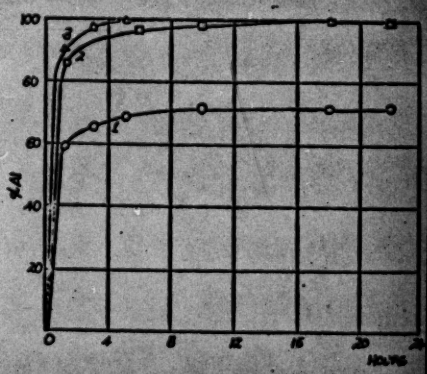


Fig. 2. Scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkage with 20% hydrochloric acid: 1 - polyaluminoxytetra (dimethylphenyldisiloxane) 2 - nonaethylaluminoxytrisiloxane; 3 - kaolin

The results presented in Fig. 2 show that, under the action of 20% hydrochloric acid for one hour, the $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkages in polyaluminoxytetra(dimethylphenyldisiloxane) are broken down to the extent of 59.9%, those in nonaethylaluminoxytrisiloxane to the extent of 86.7% and those in kaolin to the extent of 87.8%. After five hours the corresponding figures are 69.0, 98.7, and 100%, and after ten hours the extent of scission is 72.0% for polyaluminoxytetra (dimethylphenyldisiloxane) and 99.2% for nonaethylaluminoxytrisiloxane. The results presented in Fig. 3 show that, under the action of 30% hydrochloric acid for one hour, the $-\overset{|}{Si}-O-\overset{|}{Al}-$ -linkages in polyaluminoxytetra(dimethylphenyldisiloxane) are broken down to the extent of 67.2%, those in nonaethylaluminoxytrisiloxane to the

extent of 93 1%, and those in kaolin to the extent of 100%. After ten hours the first two figures are raised to 72 and 100%, respectively.

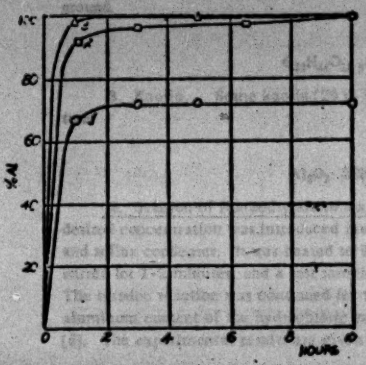
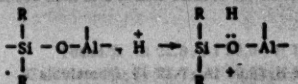
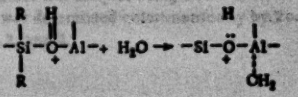


Fig. 3. Scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ linkage with 30% hydrochloric acid: 1 - polyaluminoxytetra(dimethyl--phenyldisiloxane); 2 - nonaethylaluminoxytrisiloxane; 3 - kaolin

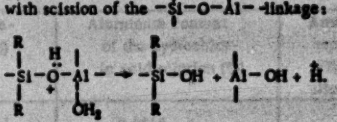
The scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ linkage in polyorganometallosiloxanes proceeds in accordance with the following mechanism: In the first stage a proton reacts with the oxygen of the aluminosiloxane linkage:



An oxonium compound is formed in which the aluminum has enhanced electrophilic activity; it reacts with water with formation of a transitional complex in accordance with the scheme:



The resulting transitional complex breaks down with scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ linkage:



Our results show that the $-\overset{|}{Si}-O-\overset{|}{Al}-$ linkage in polyaluminoxytetra(dimethylphenyldisiloxane) is more stable to the action of hydrochloric acid than the same linkage in kaolin and nonaethylaluminoxytrisiloxane. This is explained by the fact that when such reagents act upon the molecule of polyaluminoxytetra(dimethylphenyldisiloxane) two reactions occur: first the scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ linkage and then the condensation of the silicon-bound hydroxyls with one another. The second reaction leads to the formation of complex molecules of partially broken down molecules of aluminoxytetra(dimethylphenyldisiloxane), and this creates steric difficulties for the development of the first reaction.

EXPERIMENTAL

1. Synthesis of Nonaethylaluminoxytrisiloxane. A mixture of 2.7 g (0.1 mole) of aluminum turnings, 39.6 g (0.3 mole) of triethylsilanol, and 0.005 g of mercuric chloride was prepared in a round-bottomed flask fitted with reflux condenser. The mixture was heated until almost the whole of the aluminum had dissolved, the final temperature being 140°. The product was cooled and dissolved in benzene, the solution was filtered, and benzene was distilled off from a boiling water bath. In order to remove unchanged triethylsilanol, the distillation was completed under reduced pressure (85° at 5 mm). The product was 40 g of nonaethylaluminoxytrisiloxane, obtained as a crystalline substance.

$C_{18}H_{45}O_3Si_3Al$. Found%: Si 19.52; 19.13; Al 6.56; 6.56
Calculated%: Si 20.0 Al 6.7

Found M 424 (cryoscopically in benzene)
Calculated M 420

2. Synthesis of Polyaluminoxytetra(dimethylphenyldisiloxane). Solvent and aqueous alkali in which 6.67 g (0.05 mole) of aluminum chloride was dissolved were introduced into a glass vessel (hydrolyzer) having double walls for the circulation of water and provided with stirrer, thermometer, and dropping funnel. The contents of the vessel were stirred vigorously while a mixture of 51.6 g (0.4 mole) of dichlorodimethylsilane (chlorine content 55.2%; calculated value 54.98%) and 21.14 g (0.1 mole) of trichlorophenylsilane (chlorine content 50.0%; calculated value 50.3%) was added from the dropping funnel. Hydrolysis was for 90 minutes at 13.20°. The oily layer was washed

with water and distilled to remove solvent, leaving liquid polymer in 70% yield.

A portion (33 g) of the liquid polyaluminoxytetra(dimethylphenyldisiloxane) was condensed for three hours at 195-200°, air being blown through the system. A gellike product (25 g) was obtained. It was heated further for 33 hours in a thermostat at 200° in order to convert it into an infusible insoluble solid; it was then finely ground.

$C_{32}H_{44}O_{11\,5}Si_8Al$. Found%: Si 27.02; Al 3.07
Calculated%: Si 26.95; Al 3.12

3. Kaolin. Some kaolin (20 g) was heated at red heat in a muffle furnace for two hours to remove moisture.

$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Found %: Si 21.8; Al 20.0; H 1.68; C 0.8; O 55.7
Calculated%: Si 21.7; Al 20.93; H 1.55; O 55.81

4. Scission of Nonaethylaluminoxytrisiloxane with Hydrochloric Acid. Hydrochloric acid (100 g) of the desired concentration was introduced into a three-necked flask fitted with hermetically sealed stirrer, thermometer, and reflux condenser. It was heated to 96°, and 1 g of nonaethylaluminoxytrisiloxane was added. The mixture was stirred for 1-2 minutes, and a test sample (2-4 g) was then removed for the determination of aluminum content. The scission reaction was continued for ten hours, further test samples being taken at 1, 3, 5, and 10 hours. The aluminum content of the hydrochloric acid solution was determined colorimetrically by Yoe and Hill's method [6]. The experimental results are given in Tables 1, 2, and 3.

TABLE 1

Scission of Nonaethylaluminoxytrisiloxane with 10% Hydrochloric Acid

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from nonaethylaluminoxytrisiloxane (%)
1	1.0940	1	0.0515	79.00
2	1.1640	3	0.0570	85.30
3	1.4470	5	0.0620	90.50
4	1.0090	10	0.0680	91.0

TABLE 2

Scission of Nonaethylaluminoxytrisiloxane with 20% Hydrochloric Acid.

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from nonaethylaluminoxytrisiloxane (%)
1	0.9842	1	0.0561	86.50
2	1.0048	5	0.0655	98.70
3	0.7960	10	0.0686	99.20

5. Scission of Polyaluminoxytetra(dimethylphenyldisiloxane) with Hydrochloric Acid. The scission of polyaluminoxytetra(dimethylphenyldisiloxane) with hydrochloric acid was carried out by the procedure described above. At the end of the reaction the precipitate of polyaluminoxytetra(dimethylphenyldisiloxane) was filtered from the hydrochloric acid solution, washed twice with 10-ml portions of 1% hydrochloric acid, and then washed with water until there was a negative reaction for chlorine. It was then dried at 105-110° and analyzed for chlorine and silicon. The experimental results are given in Tables 4, 5, and 6.

TABLE 3

Scission of Nonaethylaluminoxytrisiloxane with 30% Hydrochloric Acid.

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from nonaethylaluminoxytrisiloxane (%)
1	0.7910	1	0.0605	93.15
2	0.6778	3	0.0658	98.10
3	0.6598	6.5	0.0676	99.10
4	0.4940	10	0.0720	100.0

TABLE 4

Scission of Polyaluminoxytetra (dimethylphenyldisiloxane) with 10% Hydrochloric Acid.

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from polyaluminoxytetra(dimethylphenyldisiloxane) (%)
1	1.2842	1	0.0175	54.40
2	1.7614	3	0.0198	60.91
3	1.9152	5	0.0216	65.14
4	0.8714	10	0.0239	69.70
5	2.1454	22	0.0280	79.50

TABLE 5

Scission of Polyaluminoxytetra(dimethylphenyldisiloxane) with 20% Hydrochloric Acid

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from polyaluminoxytetra(dimethylphenyldisiloxane) (%)
1	1.9708	1	0.0218	59.9
2	1.0644	3	0.0211	65.0
3	1.5122	5	0.0231	69.4
4	1.2166	10	0.0271	71.6
5	1.3400	18	0.0270	72.0
6	1.3052	22	0.0287	71.0

6. Scission of Kaolin with Hydrochloric Acid. The scission of kaolin was carried out by the procedure described above for the scission of polyaluminoxytetra(dimethylphenyldisiloxane). The experimental results are given in Tables 7, 8, and 9.

TABLE 6

Scission of Polyaluminoxytetra (dimethylphenyldisiloxane) with 30% Hydrochloric Acid

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from polyaluminoxytetra(dimethylphenyldisiloxane(%)
1	0.8883	1	0.0190	67.2
2	1.3996	3	0.0232	71.7
3	1.1178	5	0.0246	71.7
4	1.0810	10	0.0254	71.7

TABLE 7

Scission of Kaolin with 10% Hydrochloric Acid

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from kaolin (%)
1	1.7428	1	0.2065	93.46
2	1.7626	5	0.221	96.5
3	1.3174	10	0.240	100.0

TABLE 8

Scission of Kaolin with 20% Hydrochloric Acid

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from kaolin (%)
1	1.4740	1	0.200	90.57
2	2.3204	3	0.245	97.4
3	2.0792	5	0.264	100

TABLE 9

Scission of Kaolin with 30% Hydrochloric Acid

Test No.	Weight of hydrochloric acid solution (g)	Duration of reaction (hours)	Aluminum content of the hydrochloric acid solution (%)	Amount of aluminum separated from kaolin (%)
1	1.4562	1	0.223	100
2	1.6364	3	0.275	100
3	2.1752	5	0.279	100

SUMMARY

1. Polyaluminoxytetra(dimethylphenyldisiloxane) was synthesized.

2. An investigation was made into the scission of the $-\overset{|}{Si}-O-\overset{|}{Al}-$ linkage by the action of aqueous solutions of hydrochloric acid on polyaluminoxytetra(dimethylphenyldisiloxane), nonaethylaluminoxytrisiloxane, and kaolin.

3. A mechanism is proposed for the scission reaction, and it is shown that in polyaluminoxytetra(dimethylphenyldisiloxane) scission of the linkage is more difficult than in nonaethylaluminoxytrisiloxane and in kaolin as the result of the occurence of a second, competing condensation reaction, which results in the formation of stable $-\overset{|}{Si}-O-\overset{|}{Si}-$ linkages and thus limits the extent of the breakdown of polyaluminoxytetra(dimethylphenyldisiloxane).

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POLYMERIZATION AND COPOLYMERIZATION OF N-VINYL COMPOUNDS

COMMUNICATION 1. COPOLYMERIZATION OF 9-VINYLCARBAZOLE WITH VINYL ESTERS

S. N. Ushakov and A. F. Nikolaev

In spite of the many investigations that have been devoted to the copolymerization of unsaturated monomers, many vinyl compounds have still received very little study from this point of view. Such compounds include, for example, 9-vinylcarbazole on the one hand, and certain vinyl esters on the other. In particular, there are no data in the literature on the quantitative characterization of the activities of vinyl propionate and butyrate in copolymerization reactions with other unsaturated compounds. The only references, which are given in patents, are to the formation of copolymers with vinyl chloride [1], with abietyl crotonate [2], and with a mixture of vinyl chloride and a maleic ester [3].

The copolymerization of vinyl formate has also received very little study. Descriptions have been given of the preparation of copolymers with ethylene glycol maleic ester [4], acrylonitrile [5], ethylene [6], tetrafluoroethylene [7], and vinyl chloride [8]. Copolymerization constants(r) were determined only for the system vinyl formate - acrylonitrile (r_1 0.04, r_2 3.00).

In the case of vinyl acetate such constants have been determined for its copolymerization with 33 other monomers. Copolymers of vinyl acetate have been prepared in which the second component is ethylene [9], various fluorinated olefins [10], chlorotrifluoroethylene [11], diallyl succinate [12], 2-chloroacrylic acid [13], esters of higher fatty acids (e.g. stearic and others) [14], 1,1-dichloro-2,2-difluoroethylene [15], diethylene glycol maleic ester [16], cyclic disulfides [17], allylidene diacetate [18], allyl carbanilate [19], vinylpyrene [20], diallyl phenylphosphonate [21], diallyl acetal and mixtures of the monomers styrene and acrylic esters [22], acrylonitrile and fumaric acid [23], 3-buten-2-one and methyl acrylate [22], and butadiene and vinylidene chloride [24].

A few papers have been published also on the copolymerization of 9-vinylcarbazole with other vinyl compounds. The most detailed study has been devoted to copolymers with styrene [25, 29, 30] and with a mixture of styrene and acrylonitrile [26]. There are references to the formation of copolymers with fluorinated styrenes (p-fluorostyrene and 3,4-difluorostyrene) [27], isobutene [28], methyl methacrylate [29], vinylpyrene [20], vinyl ethers [30], butadiene [30], and drying oils [31].

A quantitative characterization of the tendency of 9-vinylcarbazole to copolymerize with styrene and with methyl methacrylate was made in 1949 [29]. The values of the copolymerization constants indicate that in reactions with these monomers 9-vinylcarbazole is the less active component.

	r_1	r_2
9-Vinylcarbazole - styrene	0.012	5.5
9-Vinylcarbazole - methyl methacrylate	0.20	2.0

We have studied the copolymerization of 9-vinylcarbazole with the vinyl esters of some organic acids (formic, acetic, propionic, and butyric). It was considered that such an investigation would enable us to characterize the activities of vinyl esters and to form an opinion of their applicability in copolymerizations with other monomers.

The experiments on the copolymerization of 9-vinylcarbazole with vinyl esters were carried out at 100° in presence of 0.5% of benzoyl peroxide. We studied the effect of the composition of the original mixture on the rate of copolymerization. The duration of reaction was nine hours. The results of the experiments are given in Fig. 1 and Table 1.

Rate of Copolymerization. It will be seen from Fig. 1 that, under given conditions, the rate of polymerization of the pure monomers and their mixtures falls in the homologous series of monomers: vinyl formate > vinyl acetate > vinyl propionate > vinyl butyrate. Even very small additions of vinylcarbazole to the vinyl ester sharply

reduce the rate of the process. The reduction in the rate of copolymerization continues down to a definite minimum, which is characteristic for each monomer pair. For example, in the system vinyl formate - vinylcarbazole the yield of copolymer falls from 85 to 11%, whereas in the system vinyl acetate - vinylcarbazole it falls from 65 to 5%.

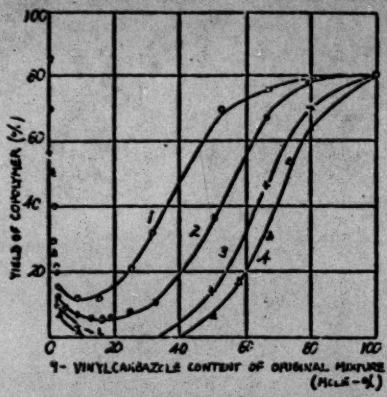

Fig. 1. Dependence of the rate of copolymerization on the 9-vinylcarbazole content of the original mixture: 1 - vinyl formate - vinylcarbazole; 2 - vinyl acetate - vinylcarbazole; 3 - vinyl propionate - vinylcarbazole; 4 - vinyl butyrate - vinylcarbazole.

With further increase in the vinylcarbazole content of the original mixture, the rate of the process increases. The minimum rate of polymerization depends on the nature of the monomer, increasing with increase in the length of the carbon chain of the acid residue of the ester and moving in the direction of a higher vinylcarbazole content in the original mixture.

In the systems vinyl propionate - vinylcarbazole and vinyl butyrate - vinylcarbazole under the time and temperature conditions of our experiments, there are definite limits of the ratio of components within which no polymerization whatever of the monomers occurs; the rate of copolymerization falls almost to zero. It would appear that vinylcarbazole, owing to the effect of the numerous double bonds of the molecule on the vinyl group, is more reactive as a monomer than vinyl esters, but the radicals of vinyl esters are considerably more reactive than vinylcarbazole. The effect of the number of double bonds in the molecule on the reactivities of some vinyl compounds was shown by Koton and Kiseleva [32], who studied the polymerization of vinylnaphthalenes. It was found that the reactivity of vinylnaphthalenes falls with reduction in the number of double bonds in the molecule. Completely hydrogenated vinylnaphthalene scarcely polymerizes at all.

As a result of the considerable rate at which the addition reaction occurs between vinylcarbazole molecules and vinyl ester radicals, polmetic vinylcarbazole radicals (the name of a polymeric radical is determined by the monomer attached at the end of the molecule) of low activity are formed even at low vinylcarbazole concentrations. Hence, the reduction in the rate of the reaction of the polymeric vinylcarbazole radical with vinyl ester molecules (there are few vinylcarbazole molecules owing to concentration conditions), as compared with the rate of addition of vinyl ester molecules to the corresponding radicals, results in a reduction in the overall rate of the copolymerization.

These considerations enable us to infer that copolymers obtained from such systems should have a lower molecular weight than polymers obtained from pure monomers. It is known that the degree of polymerization depends on the ratio of the rates of chain propagation and of chain termination, so that reduction in the rate of chain propagation must lead to a reduction in the molecular weight of the copolymers. After the attainment of a definite minimum of the rate of copolymerization (depending on the ratio of the rates of reaction between a vinylcarbazole radical and the vinyl ester and between the vinyl ester radical and the corresponding vinyl ester), the rate of copolymerization begins to rise and attains the rate of separate polymerization owing to the increase of the concentration of vinylcarbazole in the original mixture and the greater probability of the reaction between the polymeric vinylcarbazole radical and vinylcarbazole molecules. It follows also that the molecular weight of the copolymers must rise correspondingly.

The lowering observed in the rate of copolymerization of vinylcarbazole with vinyl esters is to be explained by the increase in the rate of interaction of vinyl ester radicals with vinylcarbazole in the series vinyl butyrate > vinyl propionate > vinyl acetate > vinyl formate and the consequent formation of polymeric vinylcarbazole radicals of low activity.

Copolymerization Constants. All of the systems investigated were characterized by copolymerization constants r_1 and r_2 (Table 2). These were determined graphically from the experimental data presented in Table 1.

Examining the values of $r_1 = K_{M_1 M_1} / K_{M_1 M_2}$ and $r_2 = K_{M_2 M_2} / K_{M_2 M_1}$ we see that vinylcarbazole

TABLE 1

Copolymerization of 9-Vinylcarbazole (M_2) with Vinyl Esters (M_1) in presence of 0.5% of Benzoyl Peroxide

System	Amount of monomers taken (moles × 10^2)		Molar ratio M_1^0/M_2^0	Polymerization temperature (°C)	Yield of copolymer		Nitrogen content of copolymer (%)	Composition of copolymer (moles × 10^2)		Unchanged monomers (moles × 10^2)	
	M_1	M_2			(g)	(%)		M_1'	M_2'	M_1	M_2
Vinyl Formate-vinylcarbazole	2.1911	0.2191	10.00	100	0.1008	5.04	4.00	0.0627	0.0288	2.1284	0.1903
	1.8742	0.3619	5.18	100	0.0815	3.98	3.08	0.0339	0.0296	1.8403	0.3323
	0.6947	0.7830	0.89	100	0.3885	19.30	6.68	0.0423	0.1854	0.6524	0.5976
Vinyl acetate- vinylcarbazole	1.8219	0.2263	8.05	100	0.1000	4.98	4.17	0.0494	0.0298	1.7725	0.1965
	1.3375	0.4433	3.01	100	0.1419	7.07	5.40	0.0421	0.0547	1.2955	0.3886
	0.7372	0.7160	1.03	100	0.2948	14.61	6.38	0.0411	0.1343	0.6961	0.5817
	1.8967	0.1897	10.00	65	0.0192	0.96	4.15	0.0095	0.0056	1.8872	0.1841
	0.7583	0.7161	1.06	65	0.1720	8.45	6.32	0.0260	0.0776	0.7323	0.6385
	0.4485	0.8466	0.53	65	0.5683	28.13	6.67	0.0529	0.2709	0.3956	0.5757
Vinyl propionate-vinylcarbazole	1.4400	0.2885	5.00	100	0.0105	0.53	4.70	0.0037	0.0035	1.4363	0.2850
	0.7030	0.6806	1.03	100	0.0645	3.15	5.98	0.0113	0.0276	0.6917	0.6530
	0.4030	0.8230	0.50	100	0.4770	23.82	6.40	0.0558	0.2186	0.3572	0.6044
Vinyl butyrate-vinylcarbazole	1.4957	0.1522	9.82	100	0.0314	1.57	3.81	0.0131	0.0085	1.4826	0.1437
	0.6510	0.6509	1.00	100	0.1145	5.73	5.71	0.0213	0.0467	0.6297	0.6042
	0.2306	0.9012	0.26	100	0.1830	9.13	6.58	0.0148	0.0860	0.2158	0.8152

adds to its own radical and to the radical of the vinyl ester considerably more rapidly than the vinyl ester does to its own radical and to the vinylcarbazole radical, but in the series of monomers – vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate – there is a gradual increase in the tendency for addition of vinylcarbazole monomer to the vinyl ester radical (reduction of r_1) and of the vinylcarbazole radical to vinyl ester monomer. This conclusion is confirmed by the increase in the alternation effect, determined by the product $r_1 \cdot r_2$. The lower this product, the more significant is the alternation effect. In the limiting cases the product $r_1 \cdot r_2$ is equal to zero or unity. As is known, in the first case there is true alternation, and in the second there is no alternation.

It will be seen from Table 2 that change of temperature from 65° to 100° (by 35°) causes some increase in both constants for the system vinyl acetate - vinylcarbazole. This shows that with rise in temperature both monomers become more active towards their "own" radicals. There is little change in the ratio of the constants. It may be inferred that the composition of the copolymers does not vary greatly with variation in the copolymerization temperature.

Composition of the Copolymers. In the copolymerization of two or more monomers, the product is a mixture of polymer molecules differing both in composition and in chain length. Some pairs of monomers form copolymers that are fairly homogeneous in composition, whereas other copolymers are extremely nonuniform. The compositions of vinyl acetate - vinylcarbazole copolymers were calculated by a method that one of us has used previously [33]. The original equations are those of Gindin, Abkin, and Medvedev [34]:

$$\frac{M_1}{M_1^0} = \left(\frac{M_2}{M_2^0}\right)^K \qquad K = \frac{r_1 M_1^0 / M_2^0 + 1}{r_2 + M_1^0 / M_2^0}.$$

The calculated integral and differential compositions are presented in Figures 2 and 3.

TABLE 2

Copolymerization Constants r_1 and r_2

System	Temperature (°C)	r_1	r_2	$r_1 r_2$
Vinyl formate - vinylcarbazole	100	0.196 ± 0.004	4.220 ± 0.160	0.827
Vinyl acetate - vinylcarbazole	100	0.152 ± 0.013	3.020 ± 0.240	0.465
Vinyl acetate - vinylcarbazole	65	0.126 ± 0.032	2.680 ± 0.100	0.338
Vinyl propionate - vinylcarbazole	100	0.076 ± 0.018	1.680 ± 0.140	0.128
Vinyl butyrate - vinylcarbazole	100	0.059 ± 0.020	1.280 ± 0.060	0.074

The integral-composition diagram shows the change in the mean composition of the copolymer in the course of the process, and it enables us to select the correct initial ratio of components for the preparation of a copolymer of a particular composition. Any substantial change in the composition of the copolymer occurring in the course of the copolymerization reaction, and often observed at a fairly high progress of reaction, can lead to a deterioration in the properties of the product. The differential-composition diagram provides the possibility of knowing the composition of the copolymer at any moment during the copolymerization and therefore enables us to prepare a more uniform product having better physicomechanical characteristics.

It will be seen from Figures 2 and 3 that, in the copolymerization of vinyl acetate with vinylcarbazole, the composition of the copolymer varies greatly with the degree of conversion. The greater the amount of the more active component in the original mixture, the less the variation in the composition of the copolymers. However, even with a molar ratio of vinyl acetate to vinylcarbazole of 1 : 4, the composition of the copolymer begins to vary greatly when the degree of conversion attains 65%. By application of the diagrams of integral and differential composition for this pair of monomers, it is possible to find a method of preparing copolymers that are more uniform in composition.

Distribution of the Monomeric Units in the Copolymer Macromolecule. A knowledge of the values of the copolymerization constants r_1 and r_2 enables us also to calculate the distribution of monomers in macromolecules of different composition from the formulas proposed by Gindin, Abkin, and Medvedev [34]. The relevant results cal-

culated for pairs vinyl acetate-vinylcarbazole are presented in Table 3.

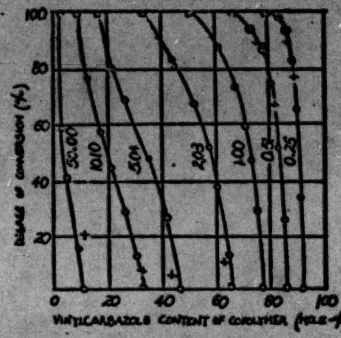

Fig. 2. Diagram of the integral compositions of copolymers calculated for the original mixtures of different compositions and for various degrees of conversion. The figures on the curves show the vinyl acetate contents of the original mixtures in moles per mole of vinylcarbazole (o-calculated values; +- experimental values)

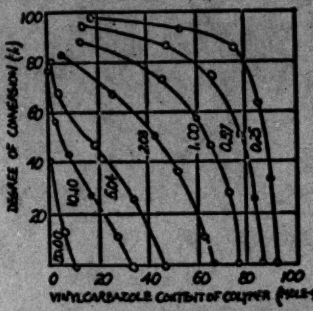

Fig. 3. Diagram of the differential composition of colpolymers calculated for original mixtures of different compositions and for various degrees of conversion. The figures on the curves show the vinyl acetate contents of the original mixtures in moles per mole of vinylcarbazole.

TABLE 3

Distribution of Monomers in the Macromolecules of Copolymers of Vinyl Acetate (M_1) and Vinylcarbazole (M_2)

Initial molar ratio M_1^0/M_2^0	Composition of copolymer (mole %)		Percentage of linkages in macromolecule				Mean length of unit	
	M_1	M_2	M_1-M_1	M_1-M_2	M_2-M_1	M_2-M_2	$\bar{L}_{M_1}$	$\bar{L}_{M_2}$
50.00	88.88	11.12	78.67	10.35	10.35	0.63	8.06	1.06
10.10	66.67	33.33	40.00	26.10	26.10	7.80	2.53	1.30
5.04	53.35	46.65	22.80	29.70	29.70	17.80	1.77	1.60
2.03	33.30	66.70	7.94	26.15	26.15	39.76	1.30	2.52
1.00	23.10	76.90	2.94	19.30	19.30	58.46	1.15	4.03
0.51	13.25	86.75	0.97	12.50	12.50	74.03	1.08	6.93
0.25	8.20	91.80	0.27	7.10	7.10	85.53	1.04	13.05

It will be seen from Table 3 that, when there is a great (e.g. 50-fold) excess of vinyl acetate in the original mixture, M_1-M_1 links predominate in the macromolecule chain, but with increase in the vinylcarbazole content of the original mixture the number of M_2-M_2 links increases at the expense of M_1-M_1 links; when there is an excess of vinylcarbazole M_2-M_2 links tend to predominate. At a molar ratio of vinyl acetate to vinylcarbazole of 1:4 and a low degree of conversion, M_1 - M_1 links are almost absent, and chain growth occurs mainly by the formation of M_1-M_2 links, and to some extent M_1-M_2 and M_2-M_2 links. Correspondingly, the mean length of the unit $\bar{L}_{M_2}$ is increased as a result of decrease in the mean length of the unit $\bar{L}_{M_1}$.

EXPERIMENTAL

Preparation of the Starting Materials. All of the monomers, with the exception of vinyl formate, were obtained from the Leningrad Polymerization Plastics Research Institute. 9-Vinylcarbazole was recrystallized three times from methanol and once from vinyl acetate; it was obtained as a white crystalline powder, m.p. 64° [bromine value 92.4 (calculated 92.5); nitrogen content 7.22% (calculated 7.25%)]. We found that the purest preparation of vinylcarbazole was obtained when it was recrystallized from vinyl acetate. Freshly recrystallized vinylcarbazole

was used in the experiments. Vinyl formate was synthesized by the liquid-phase method from anhydrous formic acid and acetylene at 40° in presence of freshly prepared 2% mercury phosphate as catalyst. The reaction product was fractionated through a laboratory column, the vinyl formate fraction boiling in the range 45.0-46.0° (760 mm) being collected. Vinyl formate and the other vinyl esters were distilled before use, and fractions collected over a narrow boiling range (0.2°) were used in the experiments. The properties of the esters are given in Table 4. Benzoyl peroxide was purified by precipitation with methanol from its solution in chloroform and by precipitation with distilled water from its solution in acetone; it was dried in a vacuum at room temperature. The benzoyl peroxide was analyzed by a method that has been verified by Kasterina and Itkina [35]. The sample used contained 99.5% of benzoyl peroxide and melted at 103.5°.

TABLE 4

Properties of Vinyl Esters

Name of ester	B.p.(° C, 760mm)	Properties		Monomer content(%)
		d_{20}^{20}	n_D^{20}	
Vinyl formate	43.0	0.9594	1.3347	99.80
Vinyl acetate	73.0	0.9343	1.3958	99.98
Vinyl propionate	94.8	0.9170	1.4028	99.50
Vinyl butyrate	116.5	0.9018	1.4092	99.70

Copolymerization Procedure. The copolymerization of vinylcarbazole with vinyl esters was carried out in the mass in 5-ml glass ampoules in an atmosphere of air, definite amounts of components being taken in order to maintain identical reaction conditions. Before use, the ampoules were treated for 24 hours with warm chromic acid mixture, washed with distilled water, steamed for three hours, and dried in a thermostat at 120°. Benzoyl peroxide was used as polymerization initiator.

The components were loaded into the ampoule in the following order: first the necessary amount of vinylcarbazole, then a weighed amount of benzoyl peroxide, and finally, after the solids had been added, a measured amount of the freshly distilled vinyl ester was added from a microburet. All the weighings were accurate within 0.0001 g. The copolymerization was carried out by placing the ampoules containing the monomer mixtures (amounting to 2 g) in a thermostat and shaking them continuously at a temperature of 100 ± 0.1°. After definite intervals of time ampoules were taken out of the thermostat and cooled in solid carbon dioxide to stop the process rapidly. The experiments for the determination of the copolymerization constants were taken to a low degree of conversion.

Isolation of Copolymers. The cooled ampoules were opened, and their contents were covered with benzene (chloroform was used for copolymers of vinylcarbazole and vinyl formate). The copolymer solutions were transferred to 100-ml flasks. The ampoules were washed with fresh portions of solvent until a drop of solvent taken from the ampoule did not produce a turbidity in petroleum ether due to precipitation of copolymer.

The polymer solution, diluted to the necessary concentration with solvent, was added dropwise with continuous stirring to a large volume of petroleum ether. The concentration of polymer necessary was determined by the precipitation conditions (the copolymer should separate in the form of light flocks, and not as conglomerates that are difficult to wash), and it depended on the composition of the copolymer and the extent of polymerization. After the precipitation of the whole of the copolymer, the solution was poured off and the precipitate was washed several times by decantation with fresh portions of precipitant. The copolymer was then again dissolved, and its precipitation was carried out according to the scheme described. The doubly reprecipitated copolymer was collected on a weighed filter and washed several times with warm petroleum ether. The filter with the precipitate was dried in the air for two hours and then placed in a vacuum cupboard. The copolymers were dried to constant weight at 60° at a residual pressure of 3-5 mm.

Analysis of the Copolymers. All of the copolymers were analyzed for nitrogen by the semimicro Kjeldahl method [36]. The compositions of the copolymers were calculated from their yields and nitrogen contents.

SUMMARY

1. Previously undescribed copolymers of 9-vinylcarbazole and vinyl esters of organic acids (formic, acetic, propionic, and butyric) were prepared by the method of mass polymerization.

2. It was shown that for identical reaction conditions the rate of copolymerization of a vinyl ester falls as the chain length of its acid residue increases.

3. Copolymerization constants were determined for the reactions of vinyl formate, vinyl acetate, vinyl propionate, and vinyl butyrate with 9-vinylcarbazole. The differential and integral compositions of copolymers formed by 9-vinylcarbazole with vinyl acetate were calculated.

4. The considerable difference found between the copolymerization constants r_1 and r_2 indicates that the copolymers must vary greatly in composition during the course of the process. In this case the calculation of integral and differential composition diagrams makes it possible to select conditions (original proportions of components, degree of conversion) under which copolymers may be prepared that are more uniform in composition.

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HYDROGEN BONDING IN 6-CAPROLACTAM AND POLYCAPROLACTAM

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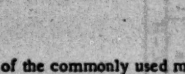
One of the commonly used methods of studying hydrogen bonding is that of infrared spectroscopy. In a substance that is associated as a result of hydrogen bonding, the OH or NH vibrations are represented by a broad displaced band, which often has an unsymmetrical complex contour with several maxima. The question arises of the physical cause of the appearance of such a contour in the absorption band. Existing concepts [1, 2, 3] are able in some measure to explain the complex character of this band. Some authors ascribe the observed maxima in the band to different types of inter- and intra-molecular hydrogen bonds. For example, Shigorin, Mikhailov, and Makaryeva [4, 5, 6], who investigated synthetic polyamides, ascribed the three observed NH-group maxima to three types of hydrogen bonds. We consider that in several cases such an approach does not reflect the essential character of the phenomenon, since one type of bond may correspond to several maxima.

EXPERIMENTAL

The present paper is devoted to an investigation of the infrared spectrum of 6-caprolactam(2-oxohexamethylenimine)  and polycaprolactam $[-NH_3(CH_2)_5CO-]_x$ in the region 2400-3400 cm^{-1}.

A solution of 6-caprolactam in carbon tetrachloride was investigated in a cell 5.5 mm in thickness having rock-salt windows. Samples of 6-caprolactam were prepared by melting the substance between two rock-salt plates. The sample was placed in a special vessel such that the absorption spectrum could be investigated both at low and high temperatures. Deuterated 6-caprolactam was also investigated, this being prepared by the action of heavy water on 6-caprolactam for 24 hours with subsequent drying over phosphoric oxide. In the NH-vibration region, 6-caprolactam in carbon tetrachloride solution has clearly marked maxima at 3400, 3280, 3220, and 3080 cm^{-1}, with a suggestion of a band at 3160 cm^{-1}. On the basis of the results on deuterated and nondeuterated 6-caprolactam in carbon tetrachloride we showed that the maxima at 3280, 3220 and 3080 cm^{-1} characterize N–H vibrations in a hydrogen-bonded group. The results are given in Tables 1 and 2 and in Fig. 1.

As will be seen, in deuterated 6-caprolactam weak maxima in the region 3400-3080 cm^{-1} are preserved and new maxima, characteristic of N–D vibrations, appear at 2520, 2460, and 2400 cm^{-1} (Fig. 1). The absorption in the 3400-3080 cm^{-1} region is associated with the presence of nondeuterated substance in solution, for which there are two possible causes: 1) the replacement of hydrogen by deuterium did not proceed to completion; 2) the deuteration process went to completion, but residual water in the carbon tetrachloride reacted with the deuterium. Measurements of the transmission of the deuterated substance showed that, with passage of time, the transmission at 3400, 3280, and 3080 cm^{-1} diminishes and that at 2520, 2460, and 2400 cm^{-1} increases. The transmission of the CH bands remains unchanged. The change in transmission with time is associated with the replacement of deuterium in 6-caprolactam by hydrogen derived from water present in the carbon tetrachloride. This process is quite complete in 24 hours (Fig. 1). This result enables us to consider that the absorption at 3400, 3280, 3220, and 3080 cm^{-1} characterizes the NH group.

It was shown by the following experiment that the maxima 3280, 3220, and 3080 cm^{-1} had been correctly assigned to the vibrations of hydrogen-bonded NH groups. The optical densities of these maxima were determined for different concentrations of 6-caprolactam in carbon tetrachloride. If a measured band were not attributable to associated groups, then for a concentration ratio of 2 the ratio of optical densities D_{c_1} / D_{c_2} would also be 2, and any departure from this value would indicate that the band is actually to be attributed to associated groups. As will be seen from Table 2, the density ratios for the maxima at 3280, 3220, and 3080 cm^{-1} are not equal to 2, whereas for the CH band at 2970 cm^{-1} the ratio is very close to 2. Hence, the first three maxima characterize the linkage N–H···O.

The sharp band at 3400 cm^{-1} which is observed only in the solution of 6-caprolactam in carbon tetrachloride, must be assigned not to an intermolecular hydrogen bond as it was previously [4], but to the vibrations of a free NH

TABLE 1

Sample	Temperature (°C)	N–H free	N–H···O					C–H						
		ν cm^{-1}	ν cm^{-1}	$\frac{I}{I_0}\cdot 100$	ν cm^{-1}	$\frac{I}{I_0}\cdot 100$	ν cm^{-1}	ν cm^{-1}	$\frac{I}{I_0}\cdot 100$	ν cm^{-1}	ν cm^{-1}	$\frac{I}{I_0}\cdot 100$	ν cm^{-1}	$\frac{I}{I_0}\cdot 100$
ε-Caprolactam	+20	–	3280	53	3200	24	3160*	3080	40	2980	2923	5	287	28
ε-Caprolactam melt	+70	–	3280	–	3240	–	–	3100	–	2980*	2923	–	2870	–
ε-Caprolactam	−150	–	3280	53	3175	16	–	3075 3060	24	2980	2923	4	2870	30
ε-Caprolactam in CCl_4 (c = 2.84 mg/ml)	+20	3400	3280	–	3220	–	3160*	3080	–	2980*	2923	–	2870	–
Polycaprolactam	+20	–	3260	14	3200	63	–	3070	68	–	2940	15	2880	25
Polycaprolactam	−150	–	3270	13	3200*	51	–	3075	53	–	2940	15	2880	25

* There is a suggestion of a band.

group. This band is not observed in crystalline and molten 6-caprolactam (Fig. 2). Its absence in molten 6-caprolactam shows that the melting of the crystals is not accompanied by hydrogen-bond rupture to any appreciable extent.

TABLE 2

(6-Caprolactam in CCl_4; d = 5.5 mm)

Vibration	ν (cm^{-1})	$\frac{D_{c_1}}{D_{c_2}}$ (c_1 = 2.84 mg/ml; $c_2 = {}^1/_2 c_1$)	$\frac{D_{c_2}}{D_{c_3}}$ (c_2 = 1.42 mg/ml; $c_3 = {}^1/_2 c_2$)
N – H	3400	1.61	1.80
	3280	2.46	2.97
	3220	2.44	2.75
	3080	2.52	3.14
C – H	2870	1.96	1.98

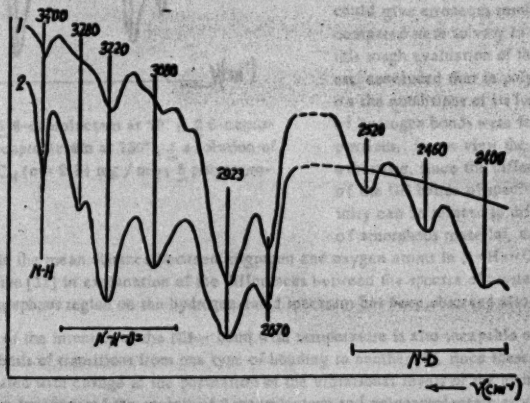


Fig. 1. Spectra 1 deuterated 6-caprolactam in CCl_4 (c = 2.84 mg/ml), and 2 the same after 24 hours.

A comparison of the absorption spectra of polycaprolactam and 6-caprolactam (Fig. 2) shows that the positions of the maxima are the same for these substances, but their intensities differ. As is known, the absorption at 3210 cm^{-1} in polycaprolactam [6] has been ascribed to an intramolecular hydrogen bond. This maximum however, exists also in 6-caprolactam, for which an intramolecular bond is excluded. Hydrogen bonds of two types are possible – in 6-caprolactam "twinning" and "catenating". We have shown, however, that there are three maxima characterizing the hydrogen bond. This example confirms the view that we expressed above, namely that it is impossible to attribute the maxima to bonds of different types. This view is confirmed also by the results of other workers [7], who observed two maxima at 3200 and 3090 cm^{-1} in a substance having only a "twinning" hydrogen bond. A particularly convincing example is provided by the absorption spectrum of 2,5-piperazinedione [8]. It was established both by X-ray [9] and by electron diffraction methods [10] that this substance contains only a "twinning" bond.

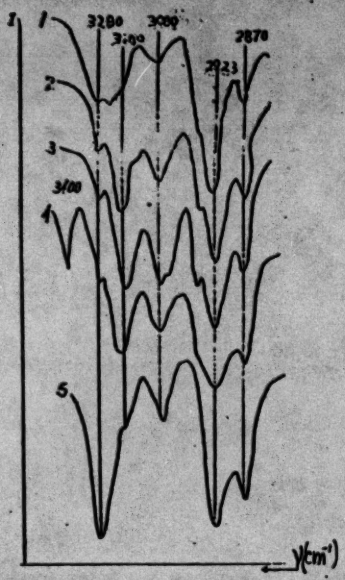
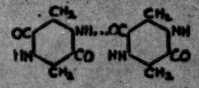


Fig. 2. Spectra of - 1 6-caprolactam at 70°; 2 6-caprolactam at 20°; 3 6-caprolactam at 150°; 4 a solution of 6-caprolactam in CCl_4 (c= 2.84 mg / ml); 5 polycaprolactam at 20°.



If it is considered that for each type of bonds there is a corresponding maximum, then in this case we should observe only one band. Experiment shows, however, that 2,5-piperazinedione gives six approximately identical maxima distributed in the region 2800-3400 cm^{-1} and corresponding to the linkage N—H···O [8]. Hence, the spectrum of 2,5-piperazinedione provides no basis for the assignment of the maximum at 3080 cm^{-1} in polycaprolactam to a "twinning" hydrogen bond, as has been done previously [6]. Shigorin and others [4, 5, 3] have investigated the variation of the intensity of the NH band in preparations of polycaprolactam varying in degree of crystallinity. They investigated also the dependence of the intensity of this band on the temperature [5]. It should be noted that the method selected for the evaluation of the intensities was a crude one and could give erroneous results if the specimens being compared were to vary in thickness. Having made this rough evaluation of the intensity, these workers concluded that in polycaprolactam, depending on the conditions of its formation, different types of hydrogen bonds were formed in different proportions. In our view the results can be interpreted otherwise, since the differences in the intensities of the NH bands of specimens differing in crystallinity can be related to differences in the proportion of amorphous material, an increase of which will lead to an increase in the mean distance between nitgrogen and oxygen atoms in N—H ···O linkages. We proposed a similar interpretation [11] in explanation of the differences between the spectra of crystalline sugar and candy. The effect of the amorphous region on the hydrogen-bond spectrum has been observed also in cellulose [12].

The variation of the intensity of the NH··· band with temperature is also incapable of being explained unequivocally on the basis of transitions from one type of bonding to another [5], since these changes can have another cause, associated with change in the population of the vibrational levels of the hydrogen bond [3]. In order to verify this view we investigated the spectra of 6-caprolactam and polycaprolactam at various temperatures. At —150° the 6-caprolactam band at 3080 cm^{-1} divides into two: 3075 and 3060 cm^{-1} (Table 1 and Fig. 2). We have observed similar phenomenon in certain organic crystalls [11]. In the 6-caprolactam melt there is a great change in the contour of the NH···band. In crystalline 6-caprolactam and in polycaprolactam hydrogen bonds are not broken in the transition from + 20° to - 150° — there is no transition of one type of bond into another, although the intensity of the NH··· vibrations and the position of the maxima vary. Thus, as the temperature is lowered the transmission of these substances at 3200 and 3080 cm^{-1} is reduced, though the transmission for the CH vibrations remains constant (Table 1). Fig. 3 gives the absorption spectrum of polycaprolactam at 20°, 150° and 220°. As the curves show, the transmission increases with rise of temperature at all of the maxima ~ 3280, 3200, and 3070 cm^{-1}. If these maxima characterized different types of hydrogen bonds [4, 5, 6] and rise of temperature brought about a transition from one type of bond to another [5], then at one maximum the transmission should increase, and at another diminish. Experiment shows that such behavior is not observed (Fig. 3).

Our results show that in the present case the variation in the intensities of the maxima with change in temperature is not associated with the transition of one type of bonds into another. Such a transition is possible in principle, but no light is thrown on such transitions by the observed temperature dependence of the differential intensity, since this dependence is characteristic of one type of bonds, the behavior being explicable on Stepanov's theory [3].

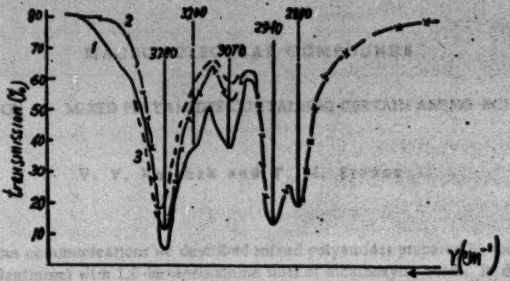


Fig. 3. Spectra of polycaprolactam: 1 - at 20°; 2 - at 150°; 3 - at 220°.

SUMMARY

1. It was shown that the maxima at 3280, 3220, and 3080 cm^{-1} observed in the absorption spectrum of 6-caprolactam characterize the vibrations of hydrogen-bonded NH groups. The band 3400 cm^{-1} given by 6-caprolactam in carbon tetrachloride solution is to be attributed to free NH groups.

2. The effect of temperature on the intensities and positions of the maxima characterizing the hydrogen bond in 6-caprolactam and polycaprolactam was investigated.

3. It was shown that the conclusions reached by some workers [4, 5, 6] regarding the existence of hydrogen bonds of three types in polycaprolactam must be regarded as doubtful.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 87. MIXED POLYAMIDES CONTAINING CERTAIN AMINO-ACID RESIDUES

V. V. Korshak and T. M. Frunze

In one of our previous communications we described mixed polyamides prepared by the reaction of ε-caprolactam (2-oxohexamethylenimine) with 1,6-hexanediamine salts of dicarboxylic acids. In this investigation we used the 1,6-hexanediamine salts of adipic, azelaic, and sebacic acids [1]. It was found that the melting points of the binary systems investigated passed through a minimum corresponding to an initial mixture containing 80 mole-% of ε-caprolactam and 20 mole-% of the 1,6-hexanediamine dicarboxylate. On the other hand, binary systems that we had investigated previously, which were derived from 1,6-hexanediamine salts of dicarboxylic acids, showed a minimum melting point for the product derived from 60 mole-% of the salt of the dicarboxylic acid having the larger number of methylene groups [2].

We have examined also the mechanism of the formation of mixed polyamides from a system containing ε-caprolactam and a diamine salt of a dicarboxylic acid, and we have shown that, depending on the proportions of the reactants and the progress of the reaction, there occur simultaneously both polymerization and polycondensation reactions; moreover, in the last stages of reaction the polymerization process no longer plays a significant role, the polyamide macromolecule being formed mainly as a result of polycondensational reactions [1].

It was of interest to determine the extent to which the regularities observed in binary systems containing ε-caprolactam retain their validity in systems containing other amino acids. With this object we have investigated systems containing 7-aminoheptanoic, 9-aminononanoic, or 11-aminoundecanoic acid as one of the original components of the reaction mixture. The second component of the system was a 1,6-hexanediamine salt of a dicarboxylic acid, namely, adipic, azelaic, or sebacic. Also, in the case of 7-aminoheptanoic acid, binary systems consisting of two amino acids were investigated, the reactants being ε-caprolactam and 7-aminoheptanoic acid.

EXPERIMENTAL

The experimental procedure and the investigation of the properties was carried out as described previously [2].

Starting Materials.

The starting materials had the following constants: 7-aminoheptanoic acid m.p. 187-188° (the literature [3] gives 183°); 9-aminononanoic acid m.p. 189-190° (the literature [4] gives 190°); 11-aminoundecanoic acid m.p. 185-186° (the literature [5] gives 186-187°). The remaining substances used had the constants given previously [1].

Results

The mixed polyamides obtained by the polycondensation of the substances indicated above, i.e., having an ω-amino carboxylic acid as one component, are white opaque horny substances. When drawn out in the molten state they readily form fibers capable of being cold-drawn. They are readily soluble in phenol, cresol, strong mineral acids, formic acid, and ethanol. Their solubilities vary over a wide range according to the relative amounts of the original components. In each system the products having the lowest melting point have the highest solubility. The dependence of the melting points of these products on the relative amounts of the components is shown in the table.

DISCUSSION OF RESULTS

As can be seen from the tabular data, the melting points of systems in which one of the original reactants is an amino acid vary with composition and pass through a minimum value. The position of the minimum is not constant, but varies according to the identities of the reactants; it corresponds to a mole fraction of 0.6-0.8 of the ω-amino carboxylic acid. The general character of the variation of the melting points is approximately the same

TABLE

Dependence of Melting Point (°C) on Composition for the Binary Systems Investigated

Names of reactants ••	Ratio of reactants •							
	1,0/0,0	0,8/0,2	0,6/0,4	0,4/0,6	0,3/0,7	0,2/0,8	0,1/0,9	0,0/1,0
HAd / Ah	250–252	236–237	208–210	173–176	–	185–186	204–205	225–230
HAz / Ah	205–208	200–202	180–182	190–192	–	204–206	213–215	225–230
HS / Ah	210–212	208–210	182–185	167–169	–	192–195	211–212	225–230
C / Ah	215–217	188–190	158–160	173–176	–	200–206	210–215	225–230
HAd / An	250–252	232–236	208–209	170–173	156–158	161–165	–	203–206
HAz / An	205–208	192–195	171–173	157–160	160–162	173–176	190–193	203–206
HS / An	210–212	195–197	180–187	165–166	160–162	160–163	180–183	203–206
C / An	215–217	175–180	130–135	150–155	–	176–182	190–195	203–206
HAd / Au	250–252	235–236	210–220	170–175	158–160	150–158	165–176	183–185
HAz / Au	205–208	195–197	160–162	138–140	135–139	142–149	–	183–184
HS / Au	210–212	200–205	180–183	150–159	139–146	145–148	–	183–185

• The ratio of reactants is given in mole fractions. The numerator and denominator refer respectively to the substances indicated as numerator and denominator in the column headed "Names of reactants".

•• Abbreviations: Ad-adipic acid; Az- azelaic acid; S- sebacic acid- H- 1,6;hexanediamine; Ah - 7;aminoheptanoic acid- An - 9;aminononanoic acid- Au - 11-aminoundecanoic acid; C - 6-capcolactam.

as in the case of the previously described binary systems containing ε-caprolactam [1], as can be readily seen from the curves for the variation of the melting points of the systems investigated with variation in composition.

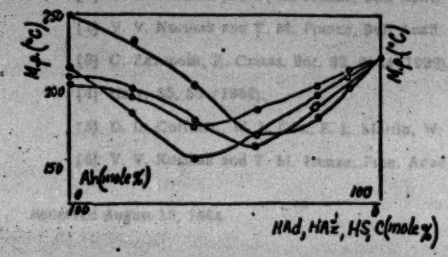

Fig. 1. Dependence of the melting points of polyamides containing 7-aminoheptanoic acid on composition: 1 - the system HAd-Ah; 2 - the system HAz-Ah; 3 - the system HS-Ah; 4 - the system C-Ah

In the case of systems derived from 7-aminoheptanoic acid and 1,6-hexanediamine salts of dicarboxylic acids (Fig. 1), it may be noted that in the system HS-Ah the lowest melting point corresponds to the product derived from a mixture containing a mole fraction of 7-aminoheptanoic acid of 0.6 (Fig. 1, Curve 3). The minimum for the system HAd-Ah also corresponds to a mole fraction of 7-aminoheptanoic acid of 0.6 (Fig. 1, Curve 1). On the other hand, the system based on the "odd" azelaic acid has a minimum at a mole fraction of 7-aminoheptanoic acid of 0.4 (Fig. 1, Curve 2), approaching the system C-Ah (Fig. 1, Curve 4) in this respect.

In the case of systems derived from 9-aminononanoic acid and diamine dicarboxylates, the system HAz-An (Fig. 2, Curve 2) has the lowest melting points in the systems containing HAd and HS correspond to a mole fraction of 9-aminononanoic acid of 0.7 (Fig. 2, Curves 1 and 3), and in the system containing HAz the minimum is at a mole fraction of 9-aminononanoic acid of 0.6 (Fig. 2, Curve 2). The system C-An differs in that the minimum is at a mole fraction of 9-aminononanoic acid of 0.4 (Fig. 2, Curve 4).

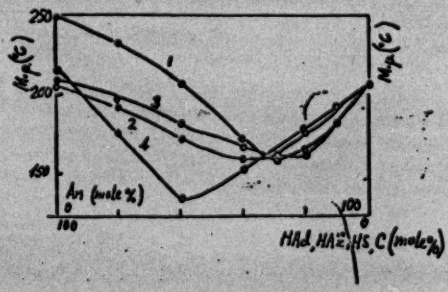

Fig. 2. Dependence of the melting points of polyamides containing 9-aminononanoic acid on composition: 1 - the system HAd-An; 2 the system HAz-An; 3 - the system HS-An; 4 - the system C-An

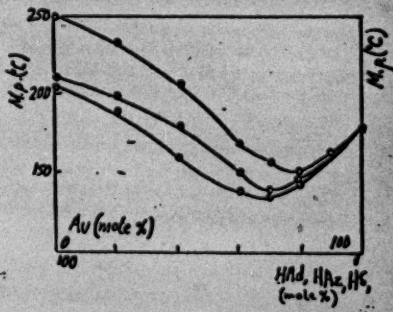

Fig. 3. Dependence of the melting points of polyamides containing 11-aminoundecanoic acid on composition: 1 - the system HAd-Au; 2 - the system HAz-Au; 3 - the system HS-Au.

In the case of systems containing 11-aminoundecanoic acid, the lowest melting point is found in the system HAz-Au (Fig. 3, Curve 2). In the HAd system the minimum corresponds to a mole fraction of 11-aminoundecanoic acid of 0.8 (Fig. 3, Curve 1). In the systems HAz-Au and HS-Au the minima correspond to a mole fraction of 11-aminoundecanoic acid of 0.7 (Fig. 3, Curves 2 and 3).

It may be noted, as a general tendency, that the melting points fall as the numbers of methylene groups in the chains of the reactants increase. For example, melting points in the systems containing 7-aminoheptanoic acid lie above those in the systems derived from 9-aminononanoic acid. Systems derived from 11-aminoundecanoic acid have still lower melting points. This kind of dependence has already been noted by us when examining the relationship between properties and structure in polyamides [6].

In conclusion we acknowledge our indebtedness to R. Kh. Freidlina and L. I. Zakharkin for placing samples of amino acids at our disposal.

SUMMARY

An investigation was made of binary systems of mixed polyamides prepared from an ω-amino acid (7-aminoheptanoic, 9-aminononanoic, or 11-aminoundecanoic acid) and 1,6-hexanediamine adipate, azelaate, or sebacate.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 58. POLYAMIDES CONTAINING ETHER LINKAGES IN THEIR MACROMOLECULAR CHAINS

V. V. Korshak and G. N. Chelnokova

Polyamides containing ether linkages in their macromolecular chains form a class of compounds that has received very little study. There are a few data on polyamides of this type in the scientific literature. Thus Hill [1] refers to a polyamide prepared from 1,5-pentanediamine and diglycolic acid. References to the preparation of polyamides from dicarboxylic acids and diamines containing ether linkages are given in various patents, which have been reviewed in articles by Somers [2].

Since polyamides containing ether linkages in their macromolecular chains are of interest not only as new members of a class of polyamides, but also because of their theoretical significance for the study of the relationship between the structure of a polymer and its properties, we undertook the preparation of several compounds of this type. The introduction of an ether linkage into the repeating unit of a polyamide macromolecule should increase the flexibility of the macromolecule and bring about changes in the properties of the polymer in the direction of increased solubility and hydrophilic character. It was of interest also to determine how the effect of the ether linkage depends on whether it is in the diamine residue or the dicarboxylic acid residue. We therefore used both reactants containing the ether oxygen in the diamine and also reactants containing the ether oxygen in the dicarboxylic acid. Also, in addition to single-component polyamides, i.e. those prepared from one diamine and one dicarboxylic acid, we prepared also mixed polyamides, i.e. copolymers obtained by the reaction of several components.

We prepared polyamides from the salts formed by 3,3'-(ethylenedioxy)-bispropylamine (ethylene glycol bis-3-aminopropyl ether) with adipic, azelaic, sebacic, and terephthalic acids, and also from the salt formed by 1,6-hexanediamine with diglycolic acid. We also carried out the polycondensation of systems of two components taken in various proportions. Two systems were investigated . 6-caprolactam with 3,3'-(ethylenedioxy)bispropylamine adipate, and 1,6-hexanediamine adipate with 3,3'-(ethylenedioxy)bispropylamine adipate.

The procedure used for the polycondensation was the same as that used previously [3]. Determinations were made of the melting points of the polyamides and of their solubilities in various solvents. The results are given in Table 1.

The polyamides obtained are flexible solids, soluble in cresol and in hydrochloric acid. Apart from the polyamide prepared from terephthalic acid, they all dissolve when heated with ethanol or 2-methoxyethanol, but the dissolved polyamide is almost entirely reprecipitated when the solutions cool. The same polyamides are slightly soluble in hot water.

The introduction of an oxygen atom into the polyamide chain results in a considerable lowering of melting point, as compared with the melting point of a polyamide in which the chain oxygen is absent but the total number of atoms in the chain is the same. For example, the polyamide prepared from glutaric acid and 1,6-hexanediamine melts at 220°, i. e. 145° higher than the polyamide prepared from diglycolic acid and 1,6-hexanediamine. In the same way, the polyamide derived from 1,10-decanediamine and adipic acid melts at 230°, whereas the polyamide derived from 3,3'-(ethylenedioxy)bispropylamine and adipic acid melts at 175-180°, i.e. 55° lower. The polyamide derived from 1,10-decanediamine and sebacic acid melts at 194°, and the polyamide derived from 3,3'-(ethylenedioxy)bispropylamine and sebacic acid melts at 157-160°, i.e. 37° lower. It is very obvious that the effect of the ether oxygen differs according to whether it forms part of the dicarboxylic acid or of the diamine. For example, the polyamide derived from diglycolic acid and 1,6-hexanediamine melts at a much lower temperature than the polyamide derived from adipic acid and 3,3'-(ethylenedioxy)bispropylamine in spite of the fact that the repeating unit of the latter is longer and contains two oxygen atoms, not one as in diglycolic acid. For the polyesters investigated by one of us in collaboration with Vinogradova [4], we showed that the introduction of each new oxygen atom

results in a proportionate lowering of the melting point of the polymer. In just the same way the lengthening of the repeating unit of the macromolecule by the introduction of methylene groups results in a lowering of the melting point, as can be readily seen even for the polyamides studied in this investigation. For example, the melting point of the polyamide derived from sebacic acid and 3,3'-(ethylenedioxy)bispropylamine is 13° lower than that of the polyamide derived from adipic acid and 3,3'-(ethylenedioxy)bispropylamine, which has a shorter repeating unit (by four methylene groups).

TABLE 1

Properties of Polyamides

Reactants		Properties of products			
Dicarboxylic acid	Diamine	M.p. (°C)*	Viscosity of 0.5% solution in cresol	Appearance	Solubility
Diglycolic	1,6-Hexanediamine	75–78	0.57	Solid	Dissolves in cresol and in hydrochloric acid. Soluble hot in alcohol; reprecipitated almost completely when solution cooled.
Adipic	3,3'-(ethylenedioxy)bispropylamine	175–180	0.40	Ditto	Dissolves in hot alcohol; reprecipitated completely when solution cooled. Slightly soluble in hot water.
Azelaic	Ditto	127–130	0.59	" "	Ditto
Sebacic	" "	157–160	0.75	" "	" "
Terephthalic	" "	236–240	0.57	" "	Dissolves in cresol and in hydrochloric acid

* These melting points were measured as follows: A piece of the polymer, approximately 3 mm x 3 mm x 1 mm, was placed in a test tube, and a layer of paraffin (about 10 mm) was introduced so as to cover completely the bulb of a thermometer placed in the tube. The test tube was placed in a glycerol bath, which was heated so that the temperature in the test tube rose at the rate of 1° per minute. The melting point was taken to be the range of temperature at the beginning of which the polymer began to be deformed (when pressed with the thermometer) and at the end of which the sample began to be capable of being drawn into a thread.

There is therefore an essential difference between the effect of an ether oxygen and a methylene group. As shown by one of us and Frunze [5], the melting point of a polyamide not containing ether linkages in the macromolecular chain depends on the ratio of the total number of methylene groups in the repeating unit to the number of amide groupings in the case of polyamides derived from dicarboxylic acids and diamines having even numbers of carbon atoms in their molecules; in the case of polyamides derived from dicarboxylic acids or diamines having odd numbers of carbon atoms in their molecules, the melting point depends on the ratio of the number of methylene groups to the number of hydrogen bonds. In these cases it is of no significance whether the methylene groups are in the dicarboxylic acid molecule or in the diamine molecule. As can be seen from the properties of the polyamides described in the present paper, there is a substantial difference between the properties of polyamides in which the ether linkage is in the dicarboxylic acid residue and those of polyamides in which the ether linkage is in the diamine residue. The ether linkage is considerably more effective when it is in the dicarboxylic acid molecule, for it brings about a greater melting point lowering than two ether linkages in the diamine molecule.

Apart from single-component polyamides, we prepared some mixed polyamides from ε-caprolactam (C) and 3,3'-(ethylenedioxy)bispropylamine adipate (EA), the ratio of reactants being varied from 1:0 to 0:1. The melting points of these mixed polyamides and the specific viscosities of their solutions are given in Table 2.

The products were almost colorless horny solids, the melts of which readily formed fibers that were capable of being cold drawn. As shown in Fig. 1, the melting points of the mixed polyamides pass through a minimum.

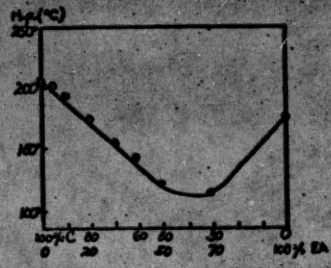

Fig. 1.

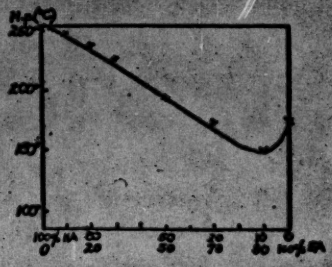

Fig. 2.

TABLE 2

Variation of the Properties of Mixed Polyamides of the System C–EA

Amount of caprolactam C (% by weight)	Amount of the salt EA (% by weight)	M.p. of polyamide(°C)	Specific viscosity of a 0.5% solution of the polyamide in cresol
100	0	207–217	0.55
95	5	202–210	0.70
90	10	196–205	0.73
80	20	173–193	0.73
70	30	155–175	0.72
60	40	145–160	0.54
50	50	123–130	0.43
30	70	115–125	0.45
0	100	175–180	0.40

TABLE 3

Amount of the salt HA (% by weight)	Amount of the salt EA (% by weight)	M.p. of polyamide (°C)	Specific viscosity of a 0.5% solution in cresol
100	0	250	—
95	5	250–260	0.34
90	10	243–250	0.42
80	20	235–240	0.49
70	30	225–231	0.70
50	50	193–200	0.45
30	70	173–183	—
10	90	150–160	—
0	100	175–180	0.40

We also investigated the system HA-EA (HA = 1,6-hexanediamine adipate). The melting points of these mixed polyamides and the specific viscosities of their cresol solutions are given in Table 3 and Fig. 2.

EXPERIMENTAL

Diglycolic Acid. Diglycolic acid was prepared from chloroacetic acid by heating it with baryta water [6]. Yield 71%; m.p. 143.5-144° (from water).

1,6-Hexanediamine Diglycolate. A solution of 19.2 (10% excess) of 1,6-hexanediamine in 5 ml of 80% ethanol was added to a solution of 20 g of diglycolic acid in 70 ml of 80% ethanol. The solution was filtered through a sintered glass filter and then set aside. The crystals that formed were filtered off and washed on the filter with

ethanol; m.p. 165-166°; yield 70%.

3,3'-(Ethylenedioxy)bispropylamine Terephthalate. A mixture of 26 g (0.148 mole) of 3,3'-(ethylenedioxy)-bispropylamine, 31 g (0.187 mole) of terephthalic acid, and 200 ml of ethanol was refluxed in a round-bottomed flask in a water bath for about 40 minutes. Water (20 ml) was added to the hot solution in order to dissolve the salt, and the mixture was filtered hot from undissolved terephthalic acid. The residue was boiled for ten minutes with a little water, and the solution obtained by filtration was added to the main filtrate. The solution was cooled and the salt was precipitated by addition of an equal volume of acetone. Two recrystallizations from ethanol gave crystals melting at 208-209°. Yield 40%.

3,3'-(Ethylenedioxy)bispropylamine Adipate. Adipic acid (8.3 g) was warmed with 20 ml of ethanol, and 10 g of 3,3'-(ethylenedioxy)bispropylamine was added gradually to the resulting solution. After being cooled and allowed to stand, the solution yielded crystals of the salt, which were filtered off, recrystallized from alcohol, and dried in the air; m.p. 119-120°; yield 66%.

3,3'-(Ethylenedioxy)bispropylamine Azelaate. This salt was prepared like the adipate; m.p. 114-116°.

3,3'-(Ethylenedioxy)bispropylamine Sebacate. This salt was prepared like the adipate; m.p. 147-148°.

In conclusion we gratefully acknowledge our indebtedness to I. N. Nazarov, who kindly placed some 3,3'-(ethylenedioxy)bispropylamine at our disposal.

SUMMARY

1. A polyamide was prepared from diglycolic acid and 1,6-hexanediamine.

2. Polyamides were prepared from 3,3'-(ethylenedioxy)bispropylamine and dicarboxylic acids, namely, adipic, azelaic, and sebacic.

3. Mixed polyamides were prepared from ε-caprolactam and 3,3'-(ethylenedioxy)bispropylamine adipate and from 1,6-hexanediamine adipate and 3,3'-(ethylenedioxy)bispropylamine adipate, the reactants being taken in various proportions.

4. It was shown that the introduction of an ether oxygen into the repeating unit of a polyamide macromolecule results in a lower melting point and a higher solubility, as compared with a polyamide having the same length of repeating unit, but not containing ether linkages.

5. It was found that an ether oxygen in the dicarboxylic acid residue brings about a much greater lowering of the melting point of the polyamide than an ether oxygen in the diamine residue.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 89. THREE-COMPONENT MIXED POLYAMIDE SYSTEMS HAVING AMINO-ACID COMPONENTS

V. V. Korshak, T. M. Frunze, and T. A. Dikareva

In a previous communication we described three-component mixed polyamide systems prepared from the components 1,6-hexanediamine adipate (HAd), 1,6-hexanediamine sebacate (HS), 1,6-hexanediamine azelaate (HAz), and 6-caprolactam (C) in the combinations HAd-HAz-HS, HAd-HS-C, HAd-HAz-C, and HS-HAz-C [1]. Investigation of the properties of these copolymers showed that as the content of each of the components was increased, the properties changed. There was a lowering of melting point and an increase in solubility. The lowest melting points and highest solubilities were found for products having compositions lying in the central part of the composition diagram.

The object of the present investigation was the study of systems containing, as one component, 7-aminoheptanoic (Ah), 9-aminononanoic (An), or 11-aminoundecanoic (Au) acid. The second and third components were selected from HAd, HS, HAz, and C, taken in various combinations. The procedure used for the polycondensation and for the investigation of the products were the same as those used previously, and the constants of the starting materials are also given in preceding communications [1-3].

EXPERIMENTAL

We investigated the following three-component systems: HAd-HAz-Ah, HAd-HS-Ah, HS-HAz-Ah, HAd-C-Ah, HS-C-Ah, HAd-C-An, HS-HAz-Au, and HAd-C-Au. We also prepared polycondensation products for the systems HAd-HAz-An, HS-HAz-An, and HAd-HAz-Au. In the last three systems we did not prepare and investigate products corresponding to all of the points on the composition diagrams, but prepared only a few products corresponding to the central part of the diagram, which were taken as being the most typical and providing a general idea of the properties of members of these three-component systems. The compositions and melting points of products derived from 7-aminoheptanoic acid are given in Table 1.

The melting points of products derived from 9-aminononanoic and 11-aminoundecanoic acids are given in Table 2.

The polyamides obtained are opaque horny solids. In the molten state they are readily drawn into threads, which are capable of being cold-drawn. The products are readily soluble in phenol, cresol, formic acid, and strong mineral acids. Some of them are soluble in ethanol.

DISCUSSION OF RESULTS

The dependence of melting point on composition is shown for the systems investigated in Figures 1-8. The general character of the dependence is similar to that found in the systems investigated previously. The lowest melting points are usually found for products having the most "central" composition. It is interesting to note that, as in systems investigated previously, there is a displacement of the regions bounded by isotherms in the direction of "odd" and longer components; this can be seen from the diagrams.

In the case of systems containing 7-aminoheptanoic acid and diamine dicarboxylates, it is noteworthy that the lowest melting point is found in the system HAd-HS-Ah (Fig. 1). It is found for compositions lying in the central part of the diagram. The region of compositions bounded by the 170° isotherm differs in form in the three diagrams (Figures 1, 2, and 3). In the system HAd-HS-Ah (Fig. 1) it is displaced in the direction of the longest component, i.e. sebacic acid. In the system HAd-HAz-Ah (Fig. 2) it is displaced in the direction of adipic acid, which is somewhat anomalous in relation to previous observations. In the system HS-HAz-Ah (Fig. 3) this region is displaced in the direction of the longest component, which is in accord with previous observations.

Systems containing ε-caprolactam in addition to 7-aminoheptanoic acid differ greatly from the preceding systems. Products corresponding to central compositions in these systems have lower melting points. Of the two systems of this type that we have investigated, HS-C-Ah (Fig. 5) has the lower minimum melting point (125°), and the 150° isotherm surrounds a larger area than in the system HAd-C-Ah (Fig. 4). In the latter system the product of lowest melting point melts at 135°; the area bounded by the 150° isotherm and by the 175° isotherm are very much smaller than in the system HS-C-Ah. In the system HAd-C-An (Fig. 6) the region of products bounded by the 150° isotherm is displaced in the direction of the amino acids; the region of products bounded by the 170° isotherm occupies a considerable fraction of the diagram.

TABLE 1

Melting Points of Three-component Copolymers • Having 7-Aminoheptanoic Acid as One Component (°C)

HAd-HAz-Ah	HAd-HS-Ah	HS-HAz-Ah	HAd-C-Ah	HS-C-Ah
198–201	200–203	182–184	182–183	154–156
60–20–20	60–20–20	60–20–20	60–20–20	60–20–20
174–179	178–190	165–166	152–153	135–137
40–40–20	40–40–20	40–40–20	40–40–20	40–40–20
162–168	174–175	171–173	155–160	150–152
20–60–20	20–60–20	20–60–20	20–60–20	20–60–20
178–180	181–182	172–174	—	145–147
50–10–40	50–10–40	50–10–40	50–10–40	50–10–40
164–166	147–154	176–178	135–137	135–142
30–30–40	30–30–40	30–30–40	30–30–40	30–30–40
180–182	153–160	186–188	133–135	133–140
10–50–40	10–50–40	10–50–40	10–50–40	10–50–40
184–186	161–162	191–192	177–180	175–178
25–25–50	25–25–50	30–10–60	30–10–60	30–10–60
165–178	171–174	190–192	173–175	171–173
30–10–60	30–10–60	20–20–60	20–20–60	20–20–60
189–191	180–181	194–196	168–170	163–166
20–20–60	20–20–60	10–30–60	10–30–60	10–30–60
194–196	187–188	206–210	154–156	149–152
10–30–60	10–30–60	10–10–80	25–25–50	25–25–50
209–210	202–203	186–187	147–150	128–130
10–10–80	10–10–80	25–25–50	35–35–30	35–35–30
	171–175	170–172	149–151	145–147
	35–35–30	35–35–30	25–50–25	25–50–25

• 1. Abbreviations: HAd 1,6-hexanediamine adipate; HAz 1,6-hexanediamine azelaate; HS 1,6-hexanediamine sebacate; C ε-caprolactam; Ah 7-aminoheptanoic acid.

2. The denominator gives the percentages by weight of the reactants in the order shown at the head of the columns. The numerator gives the melting point of the product (°C).

In the system HAd-C-Au (Fig. 7) the region of products bounded by the 150° isotherm is again displaced in the direction of the amino acids; the region bounded by the 170° isotherm is again very great. In the system HS-HAz-Au (Fig. 8) a somewhat different picture is found: the region of products bounded by the 150° isotherm is displaced toward 11-aminoundecanoic acid and is somewhat deformed in the direction of azelaic acid.

The lowest melting points found in the investigated systems (125-126°) are those of products lying in the central parts of the systems HS-C-Ah, HAd-C-Au, and HS-HAz-Au. When we compare analogous systems differing only in the amino acid, e.g. HS-HAz-Ah, HS-HAz-An, and HS-HAz-Au, it is found that with increase in the chain length of the amino acid the melting point falls for a given composition. The same applies to the system HAd-HS-Ah, HAd-HS-An, and HAd-HS-Au.

In conclusion we acknowledge our indebtedness to R. Kh. Freidlina and L. I. Zakharkin for kindly placing the amino acids at our disposal.

TABLE 2

Melting Points of Mixed Polyamides Derived from 9-Aminononanoic or 11-Aminoundecanoic Acid

[illegible]	[illegible]	[illegible]	[illegible]	HS–HAz–An	HAd–HAz–Au
187–193	185–187	185–187	170–171	165–166	185–189
60–20–20	60–20–20	60–20–20	50–10–40	50–10–40	50–10–40
163–169	167–169	147–150	155–156	149–150	147–152
40–20–40	40–20–40	40–20–40	30–30–40	30–30–40	30–30–40
153–160	178–180	135–140	157–158	148–149	139–143
20–20–60	20–20–60	20–20–60	10–50–40	10–50–40	10–50–40
171–175	160–168	160–167	155–156	142–143	140–147
50–40–10	50–40–10	50–40–10	25–25–50	25–25–50	25–25–50
138–153	146–148	134–155			160–163
30–40–30	30–40–30	30–40–30			20–60–20
138–143	146–148	126–131			
25–25–50	10–50–40	25–25–50			
133–146	125–133	142–144			
10–40–50	25–25–50	10–40–50			
148–153	145–151	142–144			
25–50–25	30–10–60	25–50–25			
163–165	141–148	168–173			
30–60–10	20–20–60	30–60–10			
163–165	139–145	156–159			
20–60–20	10–30–60	20–60–20			
163–165	168–170	169–180			
10–60–30	10–10–80	10–60–30			
173–177		182–187			
10–80–10		10–80–10			

• 1. Abbreviations other than those in Table 1: An 9-aminononanoic acid; Au 11-aminoundecanoic acid.

2. The denominator gives the percentages by weight of the reactants in the order shown at the head of the column. The numerator gives the melting point of the product (°C).

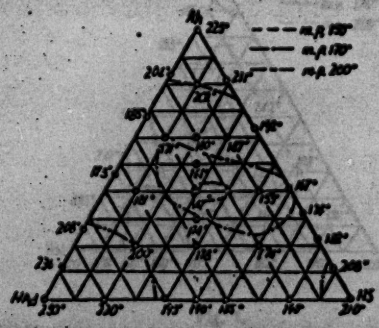

Fig. 1.

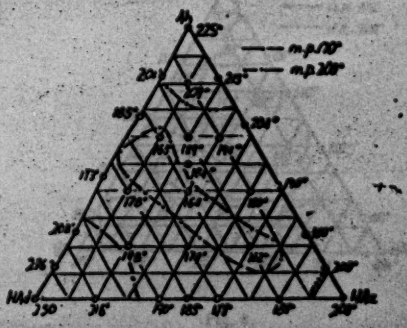

Fig. 2.

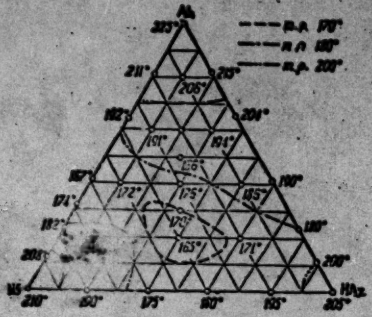

Fig. 3.

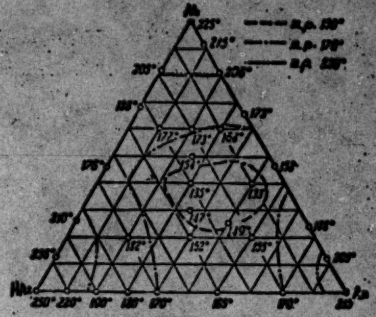

Fig. 4.

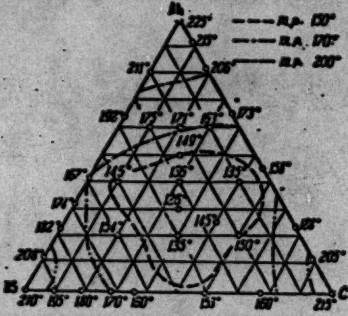

Fig. 5.

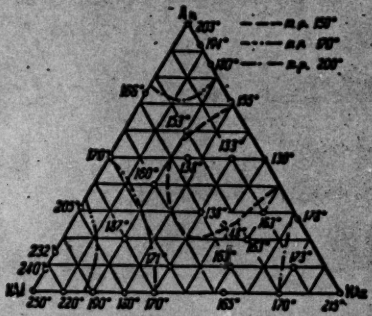

Fig. 6.

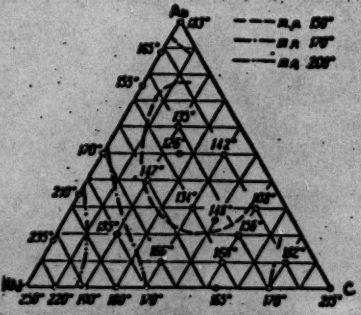

Fig. 7.

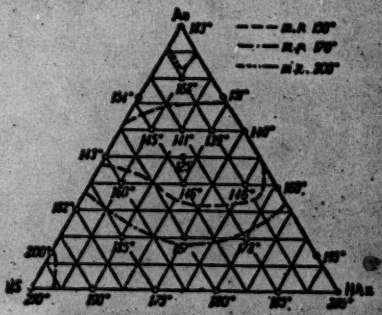

Fig. 8.

SUMMARY

1. An investigation was made of systems of mixed polyamides prepared from three components selected from 7-aminoheptanoic, 9-aminononanoic, and 11-aminoundecanoic acids, 1,6-hexanediamine adipate, azelaate, and sebacate, and 6-caprolactam.

2. It was found that the lowest melting points and highest solubilities were possessed by products lying in the central part of the composition diagram.

3. It was found that the regions bounded by isotherms were displaced in the direction of " odd " components and also in the direction of components having the longest molecules.

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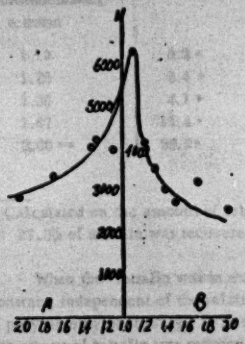
COMMUNICATION 90. POLYCONDENSATION OF 1,2-DICHLOROETHANE WITH TETRALIN

G. S. Kolesnikov, V. V. Korshak, M. A. Andreeva, and A. I. Kitaigorodsky

It was shown in a previous paper [1] that, when the catalyst concentration is low, the polycondensation of 1,2-dichloroethane with o-dichlorobenzene proceeds like that of bifunctional compounds, in spite of the fact that the potential functionality of o-dichlorobenzene is four. As we wished to determine whether the behavior found in the polycondensation of 1,2-dichloroethane with o-dichlorobenzene is general for disubstituted benzenes— which have a potential functionality of four in alkylation reactions in presence of aluminum chloride — we undertook a study of the polycondensation of 1,2-dichloroethane with tetralin (1,2,3,4-tetrahydronaphthalene). Tetralin may be regarded as an o-dialkylbenzene.



Polycondensation of 1,2-dichloroethane with tetralin; M-molecular weight; A-molar ratio dichloroethane: tetraline; B-molar ratio tetralin: dichloroethane.

In order to determine the effect of the relative amounts of the reactants on the yield and molecular weight of the polymer [poly(ar-ethylenetetralyl)], we carried out a series of experiments in which the amounts of tetralin and aluminum chloride were kept constant, but the amount of dichloroethane was varied over a wide range; the temperature and duration of the reaction were also kept constant. The amount of aluminum chloride was 10 mole% on the amount of tetralin. The procedure used for the polycondensation was the same as that used previously [2, 3], with the exception that dilution of the polycondensation products after decomposition with dilute hydrochloric acid was effected not with benzene, but with dichloroethane. The dichloroethane was distilled from the solution of polycondensation products, and further distillation under reduced pressure removed tetralin and 1,2-di-2-tetralylethane [1,2-bis(5,6,7,8-tetrahydro-2-naphthyl)ethane] which came off at 150-230° (1-2 mm). The residue was not treated further. For the purpose of molecular weight determinations, a small amount of the polymer was reprecipitated from benzene solution with methanol. The results of the experiments are given in Table 1 and in the figure. The poly(ar-ethylenetetralyl) so obtained was a brittle solid.

It will be seen from Table 1 and the figure that with reduction in the tetralin : dichloroethane ratio the molecular weight of the poly(ar-ethylenetetralyl) rises, attaining a maximum at a ratio of 1.10. Unlike the polycondensation of 1,2-dichloroethane with o-dichlorobenzene [1], reaction of equimolecular amounts of 1,2-dichloroethane and tetralin does not give a polymer of maximum molecular weight. This result is not fortuitous, for repeat experiments with equimolecular amounts of reactants gave a polymer having the same molecular weight within the limits of experimental error. Polycondensation with excess of dichloroethane resulted in a lowering of the molecular weight of the polymer to an extent that was the greater, the greater the excess of dichloroethane. In the polycondensation of 1,2-dichloroethane with tetralin, as also in the polycondensation of 1,2-dichloroethane with o-dichlorobenzene [1], the formation of three-dimensional polycondensation products was not observed even when there was a great excess of dichloroethane.

TABLE 1

Polycondensation of 1,2-Dichloroethane with Tetralin (Duration of reaction 4 hours; temperature 100°)

Molar ratio	Yield (% on amount of dichloroethane taken)		Concentration of benzene solution of poly(ar-ethyl-enetetralyl) (g/100 ml)	Specific viscosity of benzene solution	Molecular weight of the poly(ar-ethyl-enetetralyl)
	1,2-di-2-tetralylethane	poly(ar-ethyl-enetetralyl)			
Tetralin: dichloroethane					
2.00	13.1	83.6	3.014	0.088	2530
1.69	10.2	82.4	3.072	0.117	3340
1.50	9.4	81.2	3.048	0.095	2740
1.40	6.0	77.1	2.994	0.107	3140
1.30	6.4	77.5	3.116	0.126	3560
1.20	7.9	79.9	3.236	0.154	4180
1.10	3.9	80.9	3.294	0.240	6400
1.00	4.1	63.3	3.132	0.129	3620
Dichloroethane: tetralin					
1.10	5.2•	71.3•	3.076	0.140	3990
1.25	3.4•	74.1•	3.032	0.147	4250
1.30	4.1•	74.8•	3.053	0.143	4110
1.67	11.4•	65.2•	3.407	0.131	3370
2.00••	26.9•	27.2•	2.979	0.093	2740

• Calculated on the amount of tetralin taken.

•• 27.3% of tetralin was recovered unchanged.

When the tetralin was in excess, the yield of macromolecular polycondensation products remained almost constant, independent of the relative amounts of the reactants. When the dichloroethane was in excess, the yield of poly(ar-ethyleneteralyl) fell as the ratio dichloroethane: tetralin increased. As will be seen from Table 1, as the excess of tetralin was reduced, the yield of 1,2-di-2-tetralylethane fell, reaching a minimum at a dichloroethane: tetralin ratio of 1.25; further increase of this ratio resulted in an increase in the yield of 1,2-di-2-tetralylethane. It is interesting that the maximum yield of symmetrical tetrachlorobibenzyl in the polycondensation of 1,2-dichloroethane with o-dichlorobenzene was obtained at a dichloroethane: o-dichlorobenzene ratio of 1.21 [1]. This lowering of the yield of 1,2-di-2-tetralylethane, like the lowering of the yield of symmetrical tetrachlorobibenzyl, is to be explained by the reduction of the concentration of the aromatic hydrocarbon in the reaction mixture. However, the increase in the yield of the initial polycondensation product with increase in the excess of dichloroethane is, in our opinion, to be explained by the lowering of the concentration of the catalyst and reaction complex as a result of dilution with dichloroethane, which leads to a reduction in the overall rate of the process and a retardation of the process in its early stages. This then is the cause of the reduction in the yield of polymer when there is a large excess of dichloroethane. The absence of halogen (Beilstein test) in the poly(ar-ethyleneteralyl) obtained with an excess (even 100% excess) of dichloroethane indicates that excess of dichloroethane does not degrade the polymer and no products containing the CH_2CH_2Cl group are formed.

It is unexpected that a polymer of maximum molecular weight should be formed at a tetralin: dichloroethane ratio of 1.10: 1 rather than 1: 1, as observed for the reactant ratio in the polycondensation of dichloroethane and o-dichlorobenzene. One possible cause is the contamination of the tetralin with decalin, but a refractive index determination on our tetralin showed that decalin was virtually absent; the value found for n_D^{20} was 1.5416, which is almost exactly the value for pure tetralin, namely 1.54135 [4] (the determination of the refractive index has been proposed as a method for the determination of decalin in tetralin [4]). Another possible cause of the anomaly is the participation of tetralin in side reactions with a resulting reduction of its concentration in the reaction mixture.

It is known [5, 6] that tetralin, heated with small amounts (1-4%) of aluminum chloride at 30-100°, can yield benzene, octahydroanthracene, octahydrobinaphthyl, and other aromatic and hydroaromatic compounds. There can be no doubt that such reactions could occur in the polycondensation of tetralin with dichloroethane in presence of aluminum chloride at about 100°, and they would lead to a reduction in the concentration of tetralin in the reaction mixture and to a shift in the position of the molecular weight maximum for poly(ar-ethylenetetralyl).

The low-molecular-weight product obtained in the polycondensation of 1,2-dichloroethane with tetralin in presence of aluminum chloride is 1,2-di-2-tetralylethane. In order to obtain it in the pure state the product boiling at 150-230° (1-2 mm) was redistilled under reduced pressure, the fraction boiling at 190-215° (2 mm) being collected. The distillate was then crystallized twice from a 4:1 mixture of alcohol and dichloroethane, the product being a substance melting at 99-100°. Further recrystallization did not raise the melting point. The results of analysis and determination of molecular weight were in good agreement with the calculated values.

$C_{22}H_{22}$. Found %: C 90.97; 91.18; H 9.25; 9.03
Calculated %: C 90.98; H 9.02

Found M 298.2; 308.1
Calculated M 290.4

The structure of this compound, which has not been described in the literature, was established as the result of X-ray diffraction measurements. 1,2-Di-2-tetralylethane crystals prepared by the slow evaporation of an acetone solution have the form of thin square plates, ranging up to 1 sq. cm in area. Goniometric measurements and the symmetry of the X-ray pattern indicated that the crystals belonged to the prismatic class of the monoclinic syngony C_{2h}. The b axis coincides with the one diagonal of the plate, and the c axis coincides with the other. The following simple forms exist: 1) pinacoid a (100); 2) prism n (111), and 3) prism m (011).

Results of Goniometric Measurements

Face	ρ	φ	Symbol
1	90°	0°	(100)
2	90°	180°	
3	51°40'	128°37'	(111)
4	51°40'	308°37'	
5	128°20'	128°37'	
6	128°20'	308°37'	
7	45°20'	101°15'	(011)
8	45°20'	281°15'	
9	134°40'	101°15'	
10	134°40'	281°10'	

The parameters of the elementary cell, determined from oscillation photographs and Fourier analysis, are:

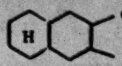
a = 13.35 ± 0.08 A
b = 8.01 ± 0.05 A
c = 7.97 ± 0.05 A
β = 101.15 ± 0°30'

Space group $P2_1/c = C^5_{2h}$. The number of molecules in the elementary cell Z = 2, i. e. the molecules are at the centers of symmetry.

The results of the X-ray-structure analysis permit us to assert that the ditetralylethane obtained is a di-2-tetralyl compound. The number of molecules in the cell taken in conjunction with the symmetry of their mutual dispositions indicates that the molecule has a center of symmetry, so that a 1-tetralyl-2-tetralyl compound is excluded. The similarity of the section bc, which contains the centers of both cyclic groups, to the sections of 2,6- and 2-derivatives of naphthalene [7] enables us to reject the di-1-tetralyl compound, which cannot be arranged geometrically into a cell of the form found.

Attempts to establish the structure of poly(ar-ethylenetetralyl) by destructive oxidation with chromic acid were

unsuccessful, and we did not succeed in isolating any of the benzenetetracarboxylic acids whose formation could be expected. The product was a mixture of acids, and attempts to separate it were unsuccessful. On the basis of the structure of the low-molecular-weight product of the polycondensation and theoretical considerations concerning the orienting effects of substituents in the benzene ring it may be supposed that in poly(ar-ethylenetetralyl) the tetralin residues are linked together through $-CH_2CH_2-$ groupings at the two β-positions of the aromatic ring of the tetralin, i.e.



With this arrangement of $-CH_2CH_2-$ groupings, each of them will be in the meta position to one of the original substituents (a CH_2 of the hydroaromatic ring) and in the para position to the other; at the same time these groupings will be ortho to each other.

In order to determine the effect of the concentration of catalyst on the yields and molecular weights of products of the condensation of 1,2-dichloroethane with tetralin, a series of experiments were carried out in which the tetralin : dichloroethane ratio (1.5 : 1), the temperature (100°), and the duration of the experiment (4 hours) were kept constant, and the catalyst concentration was varied over a wide range. The results are given in Table 2.

It will be seen from Table 2 that at first an increase in catalyst concentration leads to an increase in the yield of poly(ar-ethylenetetralyl), but when a concentration of 9-1 % (on the tetralin) is reached the yield of macromolecular products becomes almost constant. Over the range of catalyst concentrations studied, the molecular weight of the poly(ar-ethylenetetralin) remains constant, i.e. is independent of the concentration of catalyst over the range 3-12 mole-% (on the tetralin).

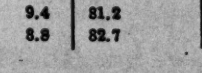
TABLE 2

Polycondensation of 1,2-Dichloroethane with Tetralin (Tetralin : dichloroethane = 1.5 : 1)

Concentration of catalyst (mole-%)		Yield (%)		Concentration of benzene solution of poly(ar-ethylenetetralyl)	Specific viscosity of benzene solution	Molecular weight of poly(ar-ethylenetetralyl)
on the tetralin	on the dichloroethane	1,2-Di-2-Tetralylethane	Poly(ar-ethylenetetralyl)			
3.0	4.5	10.8	54.4	9.626	0.321	2940
6.0	9.0	9.1	66.5	3.808	0.124	2860
6.0	13.5	8.5	82.0	3.078	0.110	3140
10.0	15.0	9.4	81.2	3.048	0.095	2740
12.0	18.0	8.8	82.7	3.646	0.128	3080

In order to check whether the solutions used for the viscosimetric determination of the molecular weight of poly(ar-ethylenetetralyl) were too highly concentrated, times of efflux were determined for benzene solutions of one of the polymers, molecular weights being calculated from the results. The results of these measurements are given in Table 3.

It will be seen from Table 3 that the molecular weight determined by the viscosimetric method does not depend on the concentration of the poly(ar-ethylenetetralyl) solution over the range 1-10 g/100 ml. Within these limits, therefore, rise in concentration does not bring about association of poly(ar-ethylenetetralyl) molecules. The experimentally determined carbon and hydrogen contents of poly(ar-ethylenetetralyl) were in close accord with the values calculated for repeating the unit:



$C_{12}H_{14}$. Calculated %: C 91.14; H 8.86 Found %: C 91.18; 91.26; H 8.74; 8.68

TABLE 3

Molecular Weight of Poly(ar-ethylenetetralyl)

Concentration of poly(ar-ethylenetetralyl) solution (g/100ml)	Specific viscosity of the solution	Molecular weight of poly(ar-ethylenetetralyl)	Concentration of poly(ar-ethylenetetralyl)solution (g/100 ml)	Specific viscosity of the solution	Molecular weight of poly(ar-ethylenetetralyl)
9.526	0.321	2940	10.119	0.346	3000
4.313	0.133	2420	5.059	0.164	2850
2.406	0.075	2750	2.529	0.083	2890
1.203	0.034	2510	1.264	0.043	3000

SUMMARY

1. A study was made of the polycondensation of 1,2-dichloroethane with tetralin in presence of aluminum chloride, and the main features of the process were established.

2. On the basis of X-ray-structure analysis it was established that the product formed in the first stage of the polycondensation of 1,2-dichloroethane with tetralin is 1,2-di-2-tetralylethane [1,2-bis(5,6,7,8-tetrahydro-2-naphthyl)ethane].

3. It was found that no three-dimensional products are formed in the polycondensation of 1,2-dichloroethane with tetralin, in spite of the fact that the potential functionality of tetralin is four.

4. It was shown that the polymer [poly(ar-ethylenetetralyl)] does not undergo association in benzene solution at concentrations of up to 10 g per 100 ml.

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[4] A. V. Lozovoi, M. K. Dyakova, and T. G. Stepantseva, J. Gen. Chem. 9, 540, (1939).

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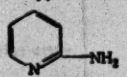
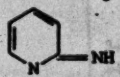
INFRARED ABSORPTION SPECTRA OF SOME BASES OF THE PYRIDINE SERIES

D. N. Shigorin, Ya. L. Danyushevsky, and Ya. L. Goldfarb

Compounds of the type of α-aminopyridine (I) and N-alkyl-α-pyridonimine (II), which contains an amidine grouping are peculiar in that they can combine stably with only one proton in their salts. It was concluded in a previous study [1] of ultraviolet absorption spectra that in bases of the first type the salt-forming center is the ring nitrogen, whereas in bases of the second type it is the side-chain nitrogen.



(I)



R (II)

It was of interest to investigate the relative basicities of the nitrogen atoms in these systems with the aid of infrared absorption spectra in the region of the vibration frequencies of the NH_2 group, so that we could examine the changes occurring in just that part of the molecule that is attacked by the proton.

The basis of this method is the known fact that in its vibration spectrum the amino group differs from the $\overset{+}{N}H_3$ group, in which a quadrivalent nitrogen atom carries a positive charge [2]. When we pass from the group to the group or the deformed amino group , the N–H bands are displaced toward the longer waves. For example, in the infrared absorption spectrum of liquid aniline the group is characterized by three bands at 3440 (8), 3357 (10), and 3220 (5) cm^{-1}. In an inert solvent and in the vapor these bands are somewhat displaced toward the shorter waves owing to the breakdown of intermolecular association through hydrogen bonds. Under these conditions the frequencies of the $-NH_2$ group have the values 3490 (10), 3410 (10), and 3230 (10) cm^{-1}. The first and second bands correspond respectively to antisymmetrical and symmetrical vibrations of the hydrogen atom with respect to the nitrogen atom. The 3220 cm^{-1} band is probably an overtone of the deformational band of the NH_2 group, which has an enhanced intensity owing to Fermi resonance [3].

In the spectrum of aniline hydrochloride, which we measured for the crystalline state in the form of a paste* there is considerable displacement of the absorption bands toward the longer waves; the shortest band has a frequency of 3100 cm^{-1}. The considerable lowering of the frequencies of the N–H vibrations in the aniline hydrochloride crystal is probably to be explained by the change in the valency state of nitrogen atom and the strong ionic interaction. Apart from these bands the aniline hydrochloride spectrum contains also an intense diffuse band at a frequency of about 2575 cm^{-1}, which probably belongs to ···HCl. The spectrum of gaseous hydrogen chloride has a clearly defined rotational structure, and from this a frequency of about 2875 cm^{-1} can be derived [3, 4]. In aniline hydrochloride, therefore, the HCl band is very much displaced toward the long waves. This may be interpreted as follows: crystalline aniline hydrochloride is a stable molecular compound, and not an ionic compound . If a true salt of the ammonium chloride type were formed, then the HCl band, as such, would not be detected. The results cited can be applied to the explanation of the results of the study of the infrared spectra of bases of the α-aminopyridine and N-alkyl-α-pyridonimine series and their salts.

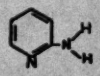
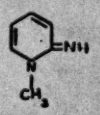
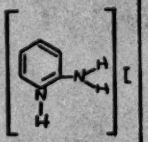
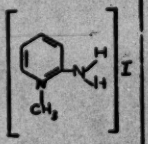
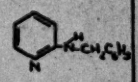
EXPERIMENTAL

The spectra were measured on a Soviet IKS-1 recording infrared spectrometer. Measurements in the 2.5–5.5

* Aniline hydrochloride was purified by sublimation.

μ region were carried out with LiF prism, and in the 5-10μ region with a rock salt prism. The frequencies were measured accurate within ± 5 cm^{-1}. The results of the measurements in the N−H region are given in Table 1.

TABLE 1 *

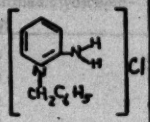
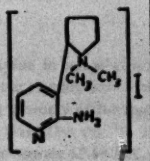
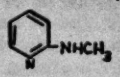
No.	Substance	Formula	NH frequencies (cm^{-1})
1	Aniline, liquid		3440(8), 3357(10), 3220(8)
	Ditto + CCl_4 (1:20)		3490(10), 3410(10), 3230(10)
2	Aniline hydrochloride, crystal		3100 cm^{-1} and lower frequencies displaced into the C−H bond region; about 2575 cm^{-1} (intense diffuse band) characterizing HCl in
3	α-Aminopyridine, crystal		3445(10, diffuse), 3306(5, diffuse), 3170(8, diffuse), 3490(10), 3395(8), 3315(2), 3170(5), 3500(10), 3410(4), 3315(4), 3175(3), 3485(8), 3362(10), 3225(1), 3485(8), 3375(10), 3210(1)
	Ditto + benzene (1:20)		
	Ditto + CCl_4 (1:20)		
	Ditto + dioxane (1:20)		
	Ditto + acetone (1:20)		
4	N-Methyl-α-pyridonimine, liquid		3335(10)
	Ditto + hexane (1:50)		3335(10)
	Ditto + dioxane (1:10		3300
5	α-Aminopyridine hydriodide, crystal		3310(2), 3235(2), 3225(4), 3120(6)
6	N-Methyl-α-pyridonimine hydriodide, crystal		3335(5), 3300(4), 3270(3), 3150(6)
7	α-Benzylaminopyridine, crystal		3230(10, diffuse)
	Ditto + dioxane		3420(10), 3292(2)
	Ditto + CCl_4		3435(10), 3260(8, diffuse)

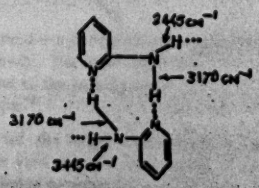
α-Aminopyridine. Three bands characterizing the NH_2 group, 3445, 3306, and 3170 cm^{-1}, were observed in the spectrum of crystalline α-aminopyridine. Its solutions in inert solvents e.g. benzene (1:20), gave two bands, 3490 (10) and 3395(8) cm^{-1} in place of the one high-frequency band 3445(10, diffuse) cm^{-1}. The 3306(5, diffuse) cm^{-1} band of crystalline α-aminopyridine preserved its value almost unchanged (3315(2) cm^{-1}). The 3170 cm^{-1} band was also preserved at high intensity, but when the inert solvent was replaced by dioxane or acetone it disappeared com-

* Continued on next page

pletely. It is probable that the interpretation of this fact is that the 3170 cm^{-1} band is due to an NH linkage participating in the formation of a dimer by hydrogen bonding:

TABLE 1 Continued

No.	Substance	Formula	NH frequencies (cm^{-1})
8	N-Benzyl-α-pyridonimine hydrochloride, crystal		3345(3), 3320(1), 3190(5), 3120(3)
9	α-Aminonicotine methiodide		3405(5), 3310(10), 3205(3)
10	α-Methylaminopyridine, liquid		3285(10, diffuse)
	Ditto + CCl_4 (1:20)		3270(10)



The association of α-aminopyridine molecules is experimentally confirmed by the results of molecular weight determinations in benzene solutions of this base at various concentrations. It will be seen from the results presented in Table 2 that the average molecular weight of α-aminopyridine rises regularly with increase in concentration.

In acetone or dioxane these dimers are broken down, and >N–H.....N< linkages are replaced by >N–H.....O, linkages, which are characterized by the frequencies 3362 and 3375 cm^{-1}, respectively, for dioxane and acetone solutions. The formation of dimers has been proved in various carboxylic acids [5], amidines [6, 7], and

other compounds. The 3445 cm^{-1} band in the spectrum of crystalline α-aminopyridine must probably be attributed to an N−H bond that takes part in weaker hydrogen bonds; the 3306 cm^{-1} corresponds to the overtone of the deformational NH_2 band, which is intensified as a result of Fermi resonance.

TABLE 2

Relative weights of α-aminopyridine and benzene	Molecular weight of α-aminopyridine (determined cryoscopically)	Relative weights of α-aminopyridine and benzene	Molecular weight of α-aminopyridine (determined cryoscopically)
1:28.0	139	1:70.0	122
1:28.3	142	1:75.6	117
1:39.0	130	1:83.0	116
1:40.5	129	1:96.5	110
1:42.5	128	1:108	110
1:50.5	126	1:149.4	111
1:52.0	125		

In dilute solutions of α-aminopyridine in nonpolar solvents (benzene, CCl_4), free NH_2 groups make their appearance with symmetrical and antisymmetrical vibrations. In particular, in carbon tetrachloride the relevant frequencies are 3500 (10) and 3410 (4) cm^{-1}, which scarcely differ from the corresponding frequencies for the NH_2 group of aniline in the same solvent [3490 (10) and 3410 (10) cm^{-1}]. Finally, the bands at 3315, 3225, and 3210 cm^{-1}, observed in solutions, probably characterize the overtone of an NH_2 group intensified by Fermi resonance.

N−Methyl-α-pyridonimine. In the NH region of the spectrum of liquid N-methyl-α-pyridonimine there is one band at 3335 (10) cm^{-1}, which characterizes the valency vibration of hydrogen with respect to the nitrogen atom in the NH group. This band does not alter in a dilute (1:50) solution in hexane, which indicates the presence of stable intermolecular hydrogen bonds. One of the authors has observed a similar phenomenon in an investigation of the vibration spectra of amidines [6, 7]. In the spectrum of a solution of M-methyl-α-pyridonimine in dioxane (1:10), a band was observed at 3300 cm^{-1}, which probably characterizes an = N−H group participating in the formation of more stable hydrogen bonds = N−H · · ·O.

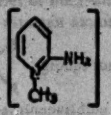
In the double bond region the frequencies 1650 (5) and 1570 (3) cm^{-1} were observed. The more intense of these probably characterizes the C = N bond [2]. The frequency 1570 cm^{-1} is probably to be associated with the system of conjugated double bonds.

α-Aminopyridine Hydriodide. The spectrum of this compound in the NH region is characterized by four bands. In spite of the fact that they differ in frequency and intensity from the bands given by crystalline α-aminopyridine, it may be concluded that in the hydriodide of this base, as in the base itself, there is an NH_2 group and that, consequently, in salt formation the proton adds to the nitrogen atom of the ring. If in fact the proton added to the side-chain nitrogenatom with formation of the group, a considerable displacement of the bands toward

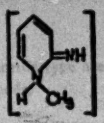
the long waves would have been observed—a displacement comparable to that observed in the comparison of the spectra of aniline and its salt (see above). The short-wave band of the hydriodide has a frequency of 3310 cm^{-1}, which differs from the short-wave band of the base by about 130 cm^{-1}, whereas in the case of aniline and its hydrochloride this difference is about 340 cm^{-1}.

The displacement of bands toward the longer waves which is observed when we compare α-aminopyridine with its hydriodide can be explained on the view that the amino group of the latter is deformed; it is probable that in such salts the positive charge is distributed between the two nitrogen atoms of the amidine grouping.

N-Methyl-α-pyridonimine Hydriodide. The spectrum of this salt contains four fairly intense bands, displaced with respect to the NH_2 bands of α-aminopyridine in the direction of the longer waves. The fact that four bands are formed already indicates that the proton unites with the side-chain nitrogen with formation of a salt of structure



I, containing a deformed NH_2 group.

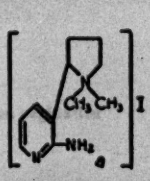
If the salt-forming center were actually the ring nitrogen atom, then the salt  I, would be

formed, and the spectrum of this would contain one or two bands characterizing the vibrations of N—H bonds, and not four bands, as found by experiment. The data in Table 1 show that a monosubstituted aminopyridine, namely α-benzylaminopyridine, does in fact give a single absorption band in the crystalline state.

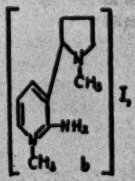
In view that N-methyl-α-pyridonimine hydriodide contains an NH_2 group is supported also by the resemblance of the spectrum of this salt to that of α-aminopyridine hydriodide. As indicated above, the bands of this group are displaced toward the longer waves; an explanation of this fact can be given on the basis of the same considerations as those given in the description of the spectrum of α-aminopyridine hydriodide (see above).

N-Benzyl-α-pyridonimine Hydrochloride. In the region of the N—H frequencies, the spectrum of this compound is similar to that of N-methyl-α-pyridonimine hydriodide. There are four bands characterizing a deformed NH_2 group: 3345 (3), 3320 (1), 3190 (5), and 3120 (3) cm^{-1}. In this case also, therefore, confirmation is found for the conclusion that the salt-forming center in systems of the type of N-alkyl-α-pyridonimine is the side-chain nitrogen atom.

α-Aminonicotine Methiodide. A study of the reactions of one of the products of the reaction of α-aminonicotine with methyl iodide showed that of the two possible structures a and b, it is necessary to assign it the structure a [8].



a



b

It was of interest to determine how far this result is in accord with the absorption of the compound in the infrared region. The data in Table 1 show that the spectrum of this compound contains three bands characterizing the N—H bonds: 3405 (5), 3310 (10), and 3205 (3) cm^{-1}. The spectra of α-aminopyridine and N-methyl-α-pyridonimine hydriodides, which have structures similar to formula b, differ from that of this methiodide; this could be explained by the deformation of the amino group in the two hydriodides. On the other hand, when the spectra of the methiodide is compared with that of crystalline α-aminopyridine, in which the amino group is free from the influence of the quadrivalent ring nitrogen atom, a close resemblance is observed, which is in full accord with structure a. In Table 1, apart from the data considered above, the frequency is given for N-methylaminopyridine, a compound isomeric with N-methyl-α-pyridonimine.

SUMMARY

1. Comparison of the infrared absorption spectra of compounds of the α-aminopyridine and α-pyridonimine series shows that the more basic nitrogen atom in these compounds is that bound by a double bond; this nitrogen atom functions as a salt-forming center.

2. It is established that in α-pyridonimine derivatives addition of a proton at the side-chain (imine) nitrogen atom results in a redistribution of electron density with formation of a molecule of "benzenoid" structure. In salts of bases of the α-aminopyridine or N-alkyl-α-pyridonimine type, the positive charge is probably distributed between both nitrogen atoms, the greater share of the charge being concentrated on the ring nitrogen in both cases. The groups formed in salts of this type differ in nature (valency state of the nitrogen atom) from the NH_2 groups of α-aminopyridine or aniline.

3. It is probable that, in the crystalline state, salts of the aniline hydrochloride type are not true salts characterized by the ionic structure $-\overset{+}{N}H_3\overline{Cl}$, but are stable saltlike molecular compounds.

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* T.p. = C. B. Translation pagination

BRIEF COMMUNICATIONS

DIPOLE MOMENTS OF DERIVATIVES OF 1,3,5-TRINITROBENZENE

E. A. Shott-Lvova and Ya. K. Syrkin

We have measured the dipole moments of 2,4,6-trinitrotoluene, 2,4,6-trinitro-m-xylene, and styphnic acid in benzene solution at 25° by the heterodyne beat method. The investigated ranges of concentration (in mole fractions) were 0.00487-0.01324, 0.00229-0.00333, and 0.00137-0.00142, respectively. Calculation by the Hedestrand method gave average values of α of 1.309, 2.742, and 2.32, respectively.

As is well known, in order to obtain the orientation polarization it is necessary to subtract the electron and atom polarizations from the total polarization P_∞. The value of R_D can be found from bond refractions. In order to determine the extrapolated value of the electron polarization it is necessary to know the refraction at various wavelengths. We carried out the extrapolation by subtracting the appropriate atomic increments, as given in the literature, from R_D. We consider that this gave us an upper limit for R_∞, since the difference between R_∞ and R_D is generally higher in aromatic derivatives than in other compounds.

In our case atom polarizations are of greater importance; they are fairly large, and if they are not taken into account high values of dipole moments may be obtained. For example, in a paper by C. Le Fevre and R. Le Fevre [1] the authors substracted R_D from P_∞ for trinitrotoluene and obtained a value of 1.37 D for the dipole moment. They regard this moment as "apparent", since the atom polarization is not taken into account.

The atom polarizations of nitro derivatives of benzene attain considerable values. For nitrobenzene Cartwright and Errera [2] obtained a value of 3.8 cc, and according to Coop [3] a value of 8.2 cc must be assumed for p-dinitrobenzene. For trinitrobenzene the difference between P_∞ and R_D is 9.6; when the refraction is extrapolated the difference is not less than 11.7. This indicates that one nitro group contributes, on the average, 4 cc. The atom polarization of toluene is 1 cc.

These considerations enable us to estimate the atom polarizations of our compounds to be 13, 14 and 12 cc, respectively. When these are compared with the atom polarizations of p-benzoquinone and chloranil [4], it appears that they will probably be close to the true values. Below we give a table showing our results. It is probable that the error in the orientation polarization is within ± 2 cc. If this is so, then the dipole moments are accurate within ± 0.04 D. The values obtained for the moments are more accurate than those obtained without any account being taken of atom polarization.

TABLE

Trinitrobenzene derivative	P_∞	R_D	R_{extrap}	P_{at}	P_{or}	$\mu \cdot 10^{18}$
$(CH_3)C_6H_2(NO_2)_3$ (1, 2, 4, 6) 2,4,6-Trinitrotoluene	87	48.7	46.5	~13	27.5	1.15± 0.04
$(CH_3)_2C_6H(NO_2)_3$ 2,4,6-Trinitro-m-xylene	135	53.3	51	~14	70	1.83± 0.03
$(HO)_2C_6H(NO_2)_3$ (1,3,2,4,6)	106.4	47.3	45.2	~12	49.2	1.5± 0.03

As can be seen from the table, the dipole moment of trinitrotoluene is almost three times as great as that of toluene. If the three nitro groups have a coplanar arrangement, their moments will cancel out. The presence of the nitro groups increases the positive charge on the hydrogens of the methyl group owing to the displacement of electrons toward the oxygen atoms and their "smearing out" over these atoms. These displacements can readily be represented either by arrows or by structural schemes. The increased electropositive character of the hydrogens is shown

also by the fact that trinitrotoluene readily reacts with the $C_6H_5O^-$ ion with formation of C_6H_5OH and the negative ion $[CH_3C_6H_2(NO_2)_3]^-$. This reaction has an activation energy of 13,600 cal [5].

The high value of the dipole moment of trinitro-m-xylene should be noted. If the two CH_3 groups are oriented at an angle of 120°, then the vector sum of their moments is equal to the moment of a single group. It would appear that, as we pass from 2,4,6-trinitrotoluene to 2,4,6-trinitro-m-xylene, the part played by the internally ionized state becomes more important

The dipole moment of resorcinol is 2.07, and the experimentally found moment for styphnic acid is less than this. This is the result of the configuration of the two hydroxyls, which form two hydrogen bonds. Under these conditions their rotation is highly inhibited.

SUMMARY

1. The dipole moments of 2,4,6-trinitrotoluene, 2,4,5-trinitro-m-xylene, and styphnic acid were measured.

2. The high values found for trinitrotoluene and trinitro-m-xylene are to be explained by the influence of the nitro groups.

3. It was shown that in these cases it is essential to take atom polarization into account.

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SELECTIVE ACTION OF CATALYSTS PREPARED FROM NICKELOUS OXIDE TREATED WITH STEAM UNDER PRESSURE

L. Kh. Freidlin, A. A. Balandin, and N. V. Borunova

We have shown recently that, when a mixture of nickelous and aluminum oxides is treated with steam under pressure, a recrystallization process occurs, and the nickel-alumina catalyst obtained from it by reduction with hydrogen is almost completely inactive in the hydrogenation of benzene at ordinary pressure.

It is known that, in presence of a nickel catalyst, double C = C and C = O bonds are more readily hydrogenated than an aromatic bond [1]. It might be expected that a catalyst prepared from a recrystallized mixture of oxides would still preserve some activity in the hydrogenation of olefins and carbonyl compounds. With this in view we investigated the possibility of hydrogenating styrene, 3-octene, and acetone in presence of such catalysts.

EXPERIMENTAL

The catalysts were prepared by coprecipitation of a mixture of molar solutions of the nitrates with 30% sodium hydroxide solution. The resulting mixture of hydroxides was washed with water and dried at 110-125°. After decomposition the composition of the oxide mixture was 35% of NiO and 65% of Al_2O_3 (or 65% of MgO). Some samples of nickelous oxide on carrier were not steam-heated; catalysts prepared from these by reduction at 350° were highly active: when benzene was hydrogenated in their presence at 120° and at a space velocity of 0.3 hr^{-1}, the extent of conversion exceeded 90%. The remainder of the samples of nickelous oxide on carriers were treated either with steam at 100 atm in an autoclave or with a mixture of steam (100 atm) and hydrogen (700 atm) in a special high-pressure reactor for five hours at 350°, and they were then reduced with hydrogen at 350° for 13-33 hours at ordinary pressure.

The activities of the catalysts in hydrogenation reactions were determined by the usual methods — in a flow system or in an autoclave. Styrene (b.p. 145-146°, n_D^{20} 1.5450), in admixture with benzene (1 : 1), was hydrogenated at 160° and at a space velocity of 0.6 hr^{-1} over a catalyst prepared from NiO/MgO which had been first treated with a mixture of steam and hydrogen for five hours. The extent to which the ethylene bond was hydrogenated, calculated from the bromine value of the catalyst, was 96.8%. The catalyzate had n_D^{20} 1.5002, i.e. the aromatic bonds were not hydrogenated (Experiment 13).

3-Octene (b.p. 123°, n_D^{20} 1.4128; and bromine value 138.7) was hydrogenated at 130° at a space velocity of 0.3 hr^{-1}. The extent of hydrogenation was determined bromometrically. Over a catalyst prepared from NiO/Al_2O_3 treated with a mixture of steam and hydrogen, 3-octene was hydrogenated to the extent of 83.9% (Experiment 3). Over a catalyst prepared from NiO/Al_2O_3 treated with steam in absence of hydrogen, 3-octene was hydrogenated to the extent of only 42.9% (Experiment 7). Over a catalyst prepared from NiO/Al_2O_3 treated with steam at the lower temperature of 300°, the extent of the hydrogenation of 3-octene was 90.1% (Experiment 9).

Piperylene (50 ml; b.p. 42-43°; n_D^{20} 1.4395) was hydrogenated at 100-150° for four hours in a rotating autoclave at an initial hydrogen pressure of 70 atm in presence of 12 g of catalyst prepared from NiO/Al_2O_3 treated with steam. The extent of the hydrogenation of the piperylene, as calculated from the bromine value of the catalyzate, was 93.2% (Experiment 6).

Acetone (b.p. 56° and n_D^{20} 1.3592) was hydrogenated at 210° at a space velocity of 0.3 hr^{-1} over a catalyst prepared from NiO/Al_2O_3 treated with a mixture of steam and hydrogen. The extent of hydrogenation, determined by the hydroxylamine hydrochloride method, was 44.3% (Experiment 11); it was 61% over a catalyst prepared from similarly treated NiO/MgO (Experiment 14). Over a catalyst prepared from NiO/Al_2O_3 treated with steam in absence of hydrogen, acetone was not hydrogenated at 150°, even under a pressure of 100 atm (Experiment 5).

As will be seen, catalysts prepared from nickelous oxide that has been recrystallized on a carrier, which are completely inactive in the hydrogenation of benzene, exhibit considerable activity in the hydrogenation of ethylene and carbonyl double bonds. It is probable that the hydrogenation of benzene is retarded owing to the inadequate power of these poorly dispersed catalysts to activate hydrogen at ordinary pressure. In order to verify this view, we carried

Selective Action of Catalysts Prepared from Steam-treated Nickelous Oxide

Expt. No.	Sample of NiO on carrier	Conditions applying during treatment for 5 hours at 350°		Duration of reduction at 350° (hours)	Substance being hydrogenated	Hydrogenation conditions		Extent of hydrogenation (%)
		Steam pressure (atm)	Hydrogen pressure			Initial hydrogen pressure (atm)	Temperature (°C)	
1	NiO/Al_2O_3 No.8	100	700	18	Benzene	Normal	180	1.2
2					Benzene	100	170	100.0
3					3-Octene	Normal	130	83.9
4	NiO/Al_2O_3 No.8	100	—	33	Benzene	100	170	0.0
5					Acetone	100	150	0.0
6					Piperylene	70	100—150	93.2
7					3-Octene	Normal	130	42.9
8	NiO/Al_2O_3 No.8*	100	—	13	Benzene	"	120	0.2
9					3-Octene	"	130	90.1
10	NiO/Al_2O_3 No.7	100	700	21	Benzene	"	120	6.0
11					Acetone	"	210	44.3
12	NiO/MgO	100	700	13	Benzene	"	180	19.0
13					Styrene	"	160	96.8
14					Acetone	"	210	61.0

* Treated with steam at 300°.

out experiments on the hydrogenation of benzene at a high pressure of hydrogen. It was found that benzene (100 g), in presence of a catalyst (15 g) prepared from NiO/Al_2O_3 previously treated with a mixture of steam and hydrogen, was not hydrogenated at 180° not only at ordinary pressure, but also at a hydrogen pressure of 40 atm. However when the hydrogen pressure was raised to 100 atm, the benzene was completely hydrogenated at 170° (Experiment 2). These results are in accord with the view that the rate of the hydrogenation of benzene over recrystallized nickelous oxide catalysts is indeed limited by the activation of the hydrogen, and not the activation of the benzene. With increase in pressure the surface occupied by the active form of hydrogen increases [2]. In presence of a catalyst prepared from NiO/Al_2O_3 treated with steam in absence of hydrogen, benzene is not hydrogenated, even under a pressure of 100 atm at 170° (Experiment 4).

Catalysts prepared from nickelous oxide treated in one case with steam and in another case with a mixture of steam and hydrogen were all equally inactive at ordinary pressure, but they varied in activity in the hydrogenation of benzene under pressure (Experiments 2 and 4). Catalysts prepared from nickelous oxide treated with steam at 300° and 350° differed in activity in the hydrogenation of 3-octene (Experiments 7 and 9).

SUMMARY

By the use of various conditions in the aging of nickelous oxide on a carrier by means of a steam treatment it is possible to control the activity of the nickel catalyst prepared from the nickelous oxide so that it loses its ability to hydrogenate an aromatic bond, but preserves its activity in the hydrogenation of double C = O bonds.

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OXIDATION POTENTIALS OF ORGANIC SULFUR COMPOUNDS •

V. G. Lukyanitsa and G. D. Galpern

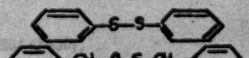
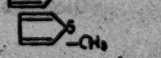
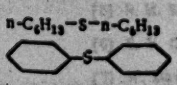
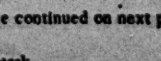
A knowledge of the values of the oxidation potentials of organic compounds is of great theoretical and practical importance, particularly for the petroleum and petrochemical industries, in which oxidative methods of purification, treatment, and alalysis have received extensive application. For the rational control of these processes it is essential that account should be taken of the oxidizabilities of the individual components of the material being treated or analyzed. A knowledge of the oxidation potentials of caustobiolites and of the rocks in which they occur is important for the solution of problems relating to the origin and metamorphism of petroleums and coals [1, 2]. Numerous workers have made not very successful attempts to determine the oxidation potentials of irreversibly oxidizable substances by indirect methods [3, 4, 5].

In the present investigation we have successfully used the differential potentiometric method recently proposed by Gorbachev and Vabel [6] for the determination of the oxidation potentials of organic sulfur compounds of various classes and certain hydrocarbons. The results that we have obtained in the investigation of 24 sulfur compounds and 5 hydrocarbons are given in the table.

It follows from the results given in the table that the oxidation potentials of sulfur compounds of different groups (thiols, sulfides, disulfides, and thiophenes) are marked off fairly clearly from one another. The variations in the values of the potentials which can be attributed to the variation in the structure of the hydrocarbon radicals attached to sulfur are considerably less than the variations from one group to another. The oxidation potential of thiophene is higher than that of its homolog, a fact that can be associated with the differences in oxidizability that have frequently been noted between these compounds [7].

The oxidation potentials of hydrocarbons were found to be considerably higher than those of the majority of the sulfur compounds. With respect to oxidation potential and rate of oxidation, the thiophenes approach the aromatic hydrocarbons. It should be noted that the rate of oxidation of hydrocarbons is considerably lower than the rate of oxidation of saturated sulfur compounds. Mesitylene and bicyclohexyl do not oxidize at all under these conditions.

TABLE

Sulfides	Irreversible Oxidation potential (v.)/ / number of oxidation equivalents per molecule	Disulfides, thiophenes, thiols	Irreversible Oxidation potential (v)/ / number of oxidation equivalents per molecule
1	2	3	4
	+ 0.342/2	n C_4H_9–S–S–n-C_4H_9	+ 0.391/4
	+ 0.346/2	i-C_4H_9–S–S–i-C_4H_9	+ 0.389/4
n-C_4H_9–S–n-C_4H_9	+ 0.352/2	i-C_5H_{11}–S–S–i-C_5H_{11}	+ 0.390/4
i-C_4H_9–S–i-C_4H_9	+ 0.368/2		+ 0.389'4
i-C_5H_{11}–S–i-C_5H_{11}	+ 0.352/2		+ 0.388/4
n-C_6H_{13}–S–n-C_6H_{13}	+ 0.358/2		+ 0.416/2
	+ 0.348/2		+ 0.409/4

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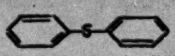
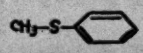
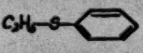
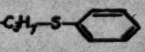
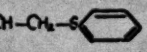
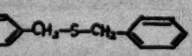
• M. V. Egorushkina and T. D. Smirnova assisted in the experimental work.

TABLE 1 (Continued)

1	2	3	4
	+ 0.361/2	n-C_9H_{19}–SH	+ 0.218/1
		Hydrocarbons	
C_2H_5–S–n-C_4H_9	+ 0.352/2	Acenaphthene	+ 0.422/2
n-C_3H_7–S–n-C_3H_{19}	+ 0.367/2	Fluorene	+ 0.432/2
	+ 0.350/2	1,2-Bibenzyl	+ 0.548/4
	+ 0.352/2	1,2-Stilbene	+ 0.441/4
	+ 0.353/2	Triphenylmethane	+ 0.576/2
	+ 0.357/2	Mesitylene and bicyclohexyl did not oxidize under the given conditions	
	+ 0.362/2		

Within the limits in which oxidizabilities of organic compounds are determined by their oxidation potentials, it must be regarded as theoretically possible to effect the selective oxidation of sulfur compounds in presence of aromatic hydrocarbons. It is also possible to effect the selective oxidation of particular groups in sulfur compounds. In particular, the present investigation has provided a theoretical basis for the oxidative method for the determination of sulfides in various petroleum products in presence of sulfur compounds of other groups [8, 9].

SUMMARY

It was established for the first time that the irreversible oxidation potentials of thiols are about + 0.2, the values for sulfides + 0.35, for disulfides + 0.39, for thiophenes + 0.41, for di- and tri-cyclic aromatic hydrocarbons from + 0.42 to + 0.58, and for hydrocarbons of the benzene series above + 0.58.

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Petroleum Institute of the Academy of Sciences of the USSR

CURRENT EVENTS

THIRD ALL-UNION CONFERENCE ON PHYSICOCHEMICAL ANALYSIS

The Third All-Union Conference on Physicochemical Analysis, which was arranged by the N. S. Kurnakov Institute of General and Inorganic Chemistry and the A. A. Baikov Institute of Metallurgy of the Academy of Sciences of the USSR, took place in Moscow on June 1-4. The conference was devoted to an appraisal of the achievements of physicochemical analysis during the five years that had passed since the Second Conference and to the marking out of the directions of future development in this original branch of general chemistry, which was brought into being as the result of the efforts of Academician N. S. Kurnakov and the very eminent Soviet school of inorganic chemists that he created.

Physicochemical analysis has found extensive application in various fields of the national economy of the Soviet Union; it is a decisive, and sometimes the only, method for the study of the nature and properties of alloys, silicates, complex mineral fertilizers, and systems formed by organic substances, for the investigation of highly important manufacturing processes concerned with the treatment of mineral raw materials, and for the preparation of various salts and metals.

Without exaggeration, the conference could be called a congress of inorganic chemists. About 700 people took part in the plenary session, and of these 250 chemists came as representatives of chemical institutes and laboratories of 44 cities and industrial centers of our country.

Over 150 papers were submitted to the organizing committee, which selected 66 for discussion. Five papers were read at the two plenary sessions, and the remaining papers at the sessions of the five sections: General, Methods of Investigation, Salts, Metals, Simple Compounds and Silicates. Altogether, 117 joined in the discussions. Great interest and lively discussion were aroused by papers devoted to fundamental questions relating to the future development of physicochemical analysis and, in particular, to problems in the modern theory of solutions, to Kurnakov's teaching on daltonides and berthollides, on the chemical individual, on the use of new methods in physicochemical analysis, etc. It was pointed out in Academician G. G. Urazov's paper "The Present State of Physicochemical Analysis and the Directions of its Future Development" and in other papers read and discussed at the conference that in the last five years a very large amount of work had been done by a team of chemists of the school of physicochemical analysis in the performance of the historic tasks set by the Nineteenth Congress of the Communist Party and under the guidance of the resolutions of the Party and the Government on the further development of industry and agriculture. The theory and methods of physicochemical analysis have been extensively applied by various research institutes, universities, and works laboratories of our country for the solution of scientific and practical problems.

Important results have been obtained in the study of the phase diagrams of light, rare, and refractory metals, and some new methods have been developed for the preparation of certain metals in a state of high purity. Physicochemical investigations have been made of the natural salts from new sources in the Kazakh, Povolzhe, Tuva, Kirghiz and other districts with the object of providing a scientific basis for the treatment of the natural salts and their utilization in the national economy. Fusion diagrams of anhydrous salts have been investigated in connection with their application as heat carriers in quenching baths and for other purposes. Some new methods for the preparation of peroxy compounds have been worked out.

During the last five years, six volumes of the Bulletin of the Sector of Physicochemical Analysis have been published, and these contained about 250 original papers in the field of physicochemical analysis. Some monographs and general reviews have also been published on the physicochemical analysis of metals and alloys and of salts of organic systems, and on other topics.

In addition to these achievements in the field of physicochemical analysis, some shortcomings were also noted by the conference. Insufficient attention has been devoted to the structure of phases of different compounds of variable composition and to the study of the crystal structures of alloys and semiconductors. Very important new methods in which labeled atoms, electron microscopy, X-ray diffraction at high and low temperatures, etc, are applied, are being adopted very slowly in scientific research. The investigation of alloys having special physical properties (heat-

stable alloys, semiconductors, alloys of rare-earth metals, etc.) is to a large extent lagging behind the requirements of the national economy and of modern technology. Insufficient attention has been given to the scientific basis of the chemical-complex treatment of mineral salts and ores.

At the plenary sessions very lively discussions followed the extremely interesting papers by Prof. B. M. Kedrov (The Subject Matter of Physicochemical Analysis, and Its Place in Science), by Prof. V. K. Semenchenko (Fundamental Problems in the Modern Theory of Solutions), by Prof. G. B. Boky (N. S. Kurnakov's Teaching on Daltonides and Berthollides in the Light of E. S. Fedorov's Theory of Crystal Structure), and by Prof. B. F. Ormont (The Theory of the Chemical Individual and some Fundamental Laws of Chemistry). The discussion on Prof. Boky's paper was continued at the Section of Physicochemical Analysis of the Scientific Council of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR. Some of the fundamental questions of physicochemical analysis dealt with in the papers had been discussed previously at special conferences arranged in recent years by the Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR on the subjects of Solid Solutions (1944), The Theory of Alloys (1952), The Definition of the Concept of the Chemical Compound (1953), and Crystal Chemistry (1953). At the conference on crystal chemistry the matters discussed included the systematics of intermetallic phases and the crystal chemistry of solid solutions. It must be pointed out, however, that these discussions have, as yet, received very little consideration in our chemical journals.

Many of the papers read at the sectional sessions were received with great interest and prompted a lively exchange of opinions. We must mention in particular interesting papers on the physicochemical analysis of solutions (N. A. Izmailov), the structure of solutions (O. Ya. Samoilov and M. I. Shakhparonov), the chemical nature of substances (D. A. Petrov), the physicochemical theory of plasticity (S. I. Gubkin), the application of radioactive indicators in physicochemical analysis (A. V. Nikolaev), the investigation of diffusion in binary alloys as a new method of physicochemical analysis (M. B . Neiman and A. Ya. Shinyaev), ultrasonics and its application in the physicochemical analysis of alloys (N. T. Gudtsov and M. N. Gavze), the physical properties of salt melts and the nature of their structural particles (N. P. Luzhnaya, N.N. Evseeva, and I. P. Vereshchetina), the character of the solubility of dolomite in water and gypsum solutions at different partial pressures of carbon dioxide (O. K. Yanatyeva), and the solubility of sparingly soluble salts in aqueous solutions of electrolytes (E. B. Shtemina and E. V. Frolova).

The conference expressed the hope that the papers and discussion would be published very promptly. Discussions of the fundamental questions of physicochemical analysis should form a feature of the new journal " Inorganic Chemistry", which is to start publication in 1956.

With a view to the development of physicochemical analysis and its application to the solution of very important scientific and national problems and with a view to the rapid application of the achievements of science in industry, the conference, in its resolutions, marked out a program for further investigations and pointed out the need that action should be taken in the following directions:

1. Research on methods of representing multicomponent systems, on the theory of chemical diagrams, and on the application of thermodynamics and statistical physics in physicochemical analysis.

2. The intensification of the experimental and theoretical study of liquid and solid solutions having metals, salts, organic substances, oxides, and silicates as components. Particular attention must be given to the structure of solutions.

3. Special attention must be turned on the application in physicochemical investigations of new methods (labeled atoms, ultrasonics, magnetic methods, optical methods, electron microscopy, and X-ray diffraction at different temperatures) for the study of phase diagrams, phase transitions, and crystal structure. One of the most important problems of the school of physicochemical analysis is to provide a collection of monographs on the methods of physicochemical analysis, and also to encourage the wider use of methods of representing complex multicomponent systems which are applicable to metallurgy, halurgy, the petrography of salts, geochemistry, hydrochemistry, and geology.

4. In the application of physicochemical analysis to the investigation of alloys -- the further development of work on the investigation of the phase diagrams, structures, and properties of heat-stable alloys, high-strength light alloys, semiconductors, and alloys of rare metals, and on the preparation of metals of high purity and the determination of their physicochemical constants.

The conference pointed out that investigations in this direction must be intensified at the A. A. Baikov Metallurgy Institute of the Academy of Sciences of the USSR, and other similar institutes and laboratories, and must be resumed at the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR.

5. In the field of the physicochemical analysis of salt systems and the investigation of natural salts – the further development of work on the study of the structures and thermodynamic properties of salts and salt melts and on the study of equilibria in aqueous salt solutions and salt melts with further increase in the number of components and in the range of the variables (temperature and pressure) determining the equilibrium.

Special attention must be paid to the physicochemical study of the rich salt deposits in the new salt-bearing districts of the country (Belorussian SSR, W. Kazakh, Povolzhe. the Eastern Provinces), and work must be continued on the investigation and utilization of the natural salts of Kara-Bogaz-Gol, Kirghiz, and the salt lakes of W. Siberia, Prikaspie, and Priaralye.

6. The further development of investigations on the scientific basis of the synthesis of peroxy compounds, boron compounds, hydrides, and other compounds, and on the study of oxides, hydroxides, carbides, nitrides, sulfides, selinides, and tellurides of various elements, particularly rare elements.

The conference resolved that it was desirable to arrange special conferences in the near future on problems in the chemistry of alloys, the physicochemical analysis of salt systems and natural salts, the chemistry of molten salts, the physicochemical analysis of peroxy compounds, and the theory of solutions. It was pointed out also that it was essential to continue the discussion of the controverial issues relating to the definition of the concept of the chemical individual, the compound, the phase, the component, etc.

In order to achieve a more extensive introduction of physicochemical analysis into the teaching practice of universities, it is necessary to widen the scope of the relevant programs and courses on general, inorganic, and physical chemistry.

A resolution carried by the conference reflected the views expressed by many participants regarding the necessity for greater coordination of investigations in the field of physicochemical analysis, which must be included in the coordination plan of the chemical institutes of the Academy of Sciences of the USSR, the Academies of Sciences of the various republics, branch institutes, and laboratories carrying out research in this direction.

The conference called upon scientists working in the field of physicochemical analysis to strengthen still more the link between science and industry and, in collaboration with industrial workers, press on still more arduously with the introduction of scientific achievements and the application of modern technology in the service of the national economy.

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UNUSUAL VALENCIES OF SOME METALS

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(Paper Read at a General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, October 27, 1955)

In the well known classical treatment, the term "valency", applied to a given element, is understood to refer merely to the number of valency bonds (usually covalent bonds) formed by an atom of the element with other atoms in the molecule. However, in inorganic chemistry there is also the old and firmly established concept of positive and negative valency, which characterizes numerically the assumed degree of oxidation of the given atom in the chemical compound. These two definitions of valency are not always equivalent; we have, for example, the hydrogen peroxide molecule H–O–O–H, in which oxygen is bivalent in the first sense and negatively univalent in the other. In the following discussion we are concerned with the degrees of oxidation of the elements.

In recent years the study of compounds corresponding to unusual degrees of oxidation of elements, particularly metals, has been appreciably intensified. Some of the results obtained are of great interest from various points of view. In the present paper it is, of course, impossible to discuss, even briefly, all of the achievements in this field, and we shall therefore deal with only a few individual metals.

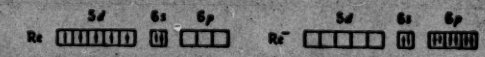
Perhaps the most interesting from the theoretical point of view is the discovery and preparation of negatively univalent rhenium. A degree of oxidation of −1, so characteristic for the halogens but never previously detected with certainty in a metal, was first established for rhenium in 1937 [1] in the product of the reduction of potassium perrhenate by amalgamated zinc in cold, very dilute solution and in complete absence of air:

$$KReO_4 + 4Zn + 5H_2SO_4 \rightarrow HRe + 4ZnSO_4 + KHSO_4 + 4H_2O.$$

The resulting solution readily reduced silver and copper salts to the metal, and the fact that Re^{1-} was indeed present in the solution was established oxidimetrically.

Further investigations by various authors [2] fully confirmed these early results, but neither hydrogen rhenide nor any of its salts were isolated until quite recently.

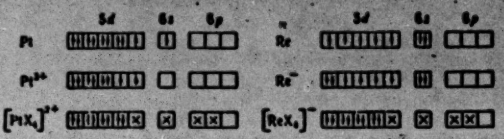
The first suggestion for the electronic structure of rhenium in this unusual state of oxidation of −1 was made by Lingane in 1942 [2], who considered that the transition from the neutral atom Re to the ion Re^- is accompanied by the following change in the structure of the outer electron shells:



However, such a mass transfer of electrons from the 5d level to the 6p level requires an enormous activation energy and is therefore extremely improbable.

A further suggestion was made in 1947 by Pauling [3], who based his treatment on the isoelectronic structure of the ions Pt^{2+} and Re^-. As it is characteristic of bivalent platinum to exist in the form of complex compounds in which it has a coordination number of four (dsp^2 hybridization), Pauling considered that the Re^- ion must be stabilized by four ligands at the corners of a square (in aqueous solution the ligands will probably be

water molecules). Pauling's structure corresponds to the following schemes of electron distribution in the outer shells:



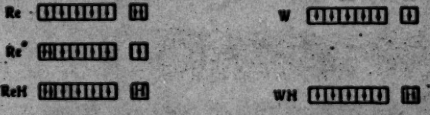
It will be seen from these schemes that the isoelectronic ions themselves – Pt^{2+} and Re^{-} are not structurally of the same type, but identity of type may be attained (if it really is attained) by the coordination of four ligands. These views imply that rhenium hydride and all of its derivatives can exist only as complex compounds, differing fundamentally in this respect from hydrogen halides and their salts.

In order to verify these concepts it was obviously necessary to prepare a rhenide in the pure state. An attempt, made in 1950, to prepare thallium rhenide [4] was not successful, but in 1952 a white precipitate containing potassium rhenide and KOH was obtained by the reduction of $KReO_4$ with potassium in a medium consisting of water and ethylenediamine (about 10% of water), the reaction being carried out in an atmosphere of nitrogen [5]. In 1954, by extraction of the caustic potash with isopropyl alcohol, the authors succeeded in obtaining a grey solid corresponding in composition approximately to $KRe \cdot 4H_2O$ (in admixture with only about 5% of KOH) [6]. They established that this substance is feebly paramagnetic, and they considered that its structure is probably that proposed by Pauling. It is interesting that a solution containing KRe can apparently be prepared also by heating the product of the direct action of potassium on rhenium with water at reduced pressure in absence of air [7].

Somewhat earlier (1953) a white crystalline lithium rhenide, readily soluble in water, was isolated, probably as a hydrate, by crystallization from an aqueous solution containing the product of the reduction of $KReO_4$ with lithium [7]. Its structure was not investigated, but it was shown that LiRe itself, and also its alkaline solutions, is quite stable in an atmosphere of nitrogen, but is slowly oxidized by air. In hydrochloric acid it rapidly reduces $BiCl_3$ to the metal, in an alkaline medium it reduces TlOH in a similar fashion, and it is oxidized quantitatively to perrhenate by acid permanganate.

These results confirm the acid character of hydrogen rhenide, which has not yet been isolated in the pure state. The question arises of for which other metals may the existence of similar compounds be most reasonably expected. One naturally turns to the nearest analogs of rhenium – technetium and manganese. However, owing to the lanthanide contraction, in the rhenium atom the effective positive field should be more powerful than in Tc and Mn atoms, i.e. the tendency of the latter to take up an electron will be less.

Tungsten – the neighbor of rhenium in the period – offers greater promise from the point of view of the possibility of the isolation of a hydride analogous to a hydrogen halide. In fact, as indicated in the schemes given below, the rhenium atom, in forming a covalent bond with hydrogen, requires activation, whereas the tungsten atom does not (and moreover, its 5d subgroup remains exactly half-full).



It should be noted also that in the tungsten atom the effective positive field is more powerful than in the rhenium atom – a fact that follows from the values of their first ionization potentials, which are 8.0 V and 7.8 V respectively (whereas for manganese the value is only 7.4 V). It would be of interest to attempt the preparation of the hydride HW and its derivatives, making use of the experience already gained in work on rhenium hydride.

The rhenium analog, manganese, and its neighbors in the period, chromium and iron, are very well known elements, and it might be thought that our knowledge of their chemistry has long been very thorough and complete. However, in recent years there have been some interesting investigations that throw new light on certain degrees of oxidation of these metals. In the following comparative table the degrees of oxidation that can be regarded as unusual are underlined:

Cr	0	<u>+1</u>	+2	+3	<u>+4</u>	<u>+5</u>	<u>+6</u>
Mn	<u>0</u>	<u>+1</u>	+2	+3	<u>+4</u>	<u>+5</u>	<u>+6</u>
Fe	<u>0</u>	<u>+1</u>	+2	+3	<u>+4</u>	<u>+5</u>	<u>+6</u>

Whereas for chromium and iron a degree of oxidation of zero has been known for a long time in the simple carbonyl derivatives $Cr(CO)_6$ and $Fe(CO)_5$, the synthesis of a manganese carbonyl was not accomplished until 1954 [8]. Volatile golden-yellow crystals of $[Mn(CO)_5]_2$ were obtained treating a suspension of MnI_2 with magnesium in ether at room temperature in presence of carbon monoxide at a pressure of 2000 atm. In composition (and structure) this compound is analogous to the rhenium carbonyl prepared in 1941 [9].

A substance that can be regarded as an intermediate compound in the transition from Mn^0 to Mn^{+1} was prepared in 1953 [10], namely, a pale-yellow substance of composition $K_{11}Mn_2(CN)_{12} \cdot 2NH_3$ or $K_4[Mn(CN)_6] \cdot K_5[Mn(CN)_6] \cdot 2NH_3$, which is precipitated when $K_4[Mn(CN)_6]$, as a solution in liquid ammonia, is reduced with potassium. The composition of the precipitate was established by analysis and by oxidimetric estimation (by reduction of Ag^+ in ammoniacal solution). As would be expected, the compound is paramagnetic (the one unpaired electron of Mn^0), but instead of the theoretical value of 1.73 magnetons, a moment of only 1.25 magnetons was found experimentally, this being explained by the authors as due to partial oxidation of the precipitate. This is a very likely explanation, but it is even more likely that the substance is not a definite stoichiometrical compound and is of variable composition, being formed by the incomplete reduction of the original complex cyanide. If this is so, then we may hope to accomplish the direct preparation of $K_5[Mn(CN)_6]$, which would not only confirm the existence of Mn compounds, but also increase the number of the "cyanyls" predicted in 1940 by Ormont [11], the first of which were nickel [12] and palladium [13] compounds of general formula $K_4[M(CN)_4]$, which were synthesized in 1942 and 1943, respectively.

The question of a degree of oxidation of +1 for manganese is not altogether clear. In 1927 [14] some colorless crystals were obtained by the vigorous reduction of a violet aqueous solution of $K_3[Mn(CN)_6]$ with aluminum powder in an atmosphere of hydrogen, and, on the basis of elementary analysis and oxidimetric estimation, these were assigned the formula $K_5[Mn(CN)_6]$. A compound of this composition should be diamagnetic, like $K_4[Fe(CN)_6]$, but it was shown in 1940 [15] that this compound has a fairly high magnetic moment (not less than 1.04 magnetons). It would appear that the substance investigated had a higher or lower degree of oxidation. It may be assumed that the compound $Mn(CO)_5I$ – prepared in 1954 [8] in the form of ruby-red crystals, readily oxidized by air, by treating manganese carbonyl with iodine – is another Mn^{+1} derivative.

The first compound of positively univalent chromium was prepared as recently as 1952 in the form of a complex compound with 2,2'-bipyridyl by reduction of a red solution of $[CrBipy_3](ClO_4)_2$ with magnesium powder, zinc dust, or sodium amalgam. The product was a blue-black powder of composition $[CrBipy_3]ClO_4$, which was insoluble in water and very readily oxidized by air. A value of 2.0-2.1 magnetons was found for its magnetic moment, which is close to the theoretically expected value of 1.73 magnetons (the discrepancy is probably due to partial oxidation). In the same year (1952), experiments were carried out on the reduction of $K_3[Cr(CN)_6]$ – as a yellow solution in liquid ammonia – with potassium, and a dark-brown precipitate was formed which, according to determinations of its reducing power (reduction of Ag^+), contained positively univalent chromium. This work, which was carried out by Colton, has not been published, but has been mentioned in a paper by other authors [17].

Iron compounds having an apparent degree of oxidation of +1 have been long known in the form of various nitroso complexes, such as $Na_2[Fe(CN)_5NO]$. The formation of some of these is accompanied by appreciable evolution of heat, this being true, for example, of the reaction:

$$2FeI_2 + 4NO \rightarrow 2Fe(NO)_2I + I_2.$$

The resulting black-brown compound volatilizes without decomposition, but is very unstable to water and air. The magnetic properties of this nitroso complex have not been studied, but some other compounds of this type

have been found to be diamagnetic in spite of the fact that Fe^{2+} ions and neutral NO molecules contain unpaired electrons. In particular, there is the red salt corresponding in composition to $K[Fe(NO)_2S]$, which is shown by X-ray analysis to be dimeric, the ion $[(NO)_2FeS_2Fe(NO)_2]^{2-}$ consisting of two tetrahedra having a common side formed by sulfur atoms, iron atoms at the centers, and NO molecules at the external corners. As it is possible in principle for the NO group to function not only as a neutral molecule, but also as a positive or negative ion (NO^+ or NO^-), it must be acknowledged that the question of the actual degree of oxidation of iron in its nitroso derivatives is still open and demands further investigation.

A cyanide complex of positively univalent iron appears to be formed by electrolytic reduction of $K_3[Fe(CN)_6]$ in solution in presence of an excess of potassium cyanide [18], but it has not been isolated. An Fe^{3+} derivative of very simple composition was prepared in 1940 [19] by the slow decomposition of the carbonyl complex of ferrous iodide in a current of carbon dioxide, which proceeds in successive stages, as follows:

$$Fe(CO)_4I_2 \rightarrow Fe(CO)_2I_2 \rightarrow Fe(CO)_2I \rightarrow FeI.$$

The final product was an extremely unstable bright-red powder; a yield of only a few milligrams was obtained, and the compound was not studied in detail. As this discussion shows, the existence of Fe^{3+} compounds has not yet been proved convincingly.

The position with regard to Fe^{4+} compounds is somewhat better, but is again not altogether clear. Already at the beginning of this century [20], black amorphous powders analyzing essentially as $BaFeO_3$ were prepared by heating mixtures of $Fe(OH)_3$ with barium or strontium hydroxide in a current of oxygen. These "perferrites" were studied further until 1952 [21], when some meta and ortho compounds of this type were prepared in the pure state not only from tervalent, but also from sexavalent iron. It was shown, in particular, that when red $BaFeO_4$ is kept, spontaneous elimination of oxygen occurs with formation of black $BaFeO_3$. The other "perferrites" that have been prepared are also black microcrystalline powders. X-Ray analysis of Ba_2FeO_4 showed that the crystals are of the same type as those of Ba_2TiO_4, which, in conjunction with elementary and oxidimetric analysis, indicates the presence of quadrivalent iron. However, the results of an investigation of the magnetic properties of these substances [21] have not yet been published. It should be noted also that both in its simple and in its complex fluorine compounds, iron fails to manifest this valency [22]. The above-mentioned salts, therefore, are as yet the only known Fe^{4+} compounds.

Chromium in the same state of oxidation (+4) was obtained in the form of its fluoride CrF_4 in 1941 by the action of fluorine on CrF_3 at 400° [23]. This substance is a fairly volatile amorphous brown substance; it deliquesces in moist air and is decomposed by water with formation of ter- and sexa-valent chromium compounds. An analogous solid brown chloride $CrCl_4$ was obtained in 1942 [24] by "freezing" a high-temperature gas-phase equilibrium, which under ordinary conditions rapidly moves in the direction $2CrCl_4 \rightarrow 2CrCl_3 + Cl_2$. In 1949 [22], a yellow complex fluoride $K_2[CrF_6]$ was prepared by the fluorination of the mixture $2KCl + CrCl_3$, and the X-ray diffraction pattern given by this substance was found to be quite analogous to that of the corresponding yellow compound of quadrivalent manganese, $K_2[MnF_6]$.

Black CrO_2, which was prepared as early as 1908 [26] by heating $Cr(OH)_3$ in the air at not above 400°, was shown by a magnetic study in 1953 [27] to be a Cr^{4+} compound, and not a basic chromium chromate $(CrO)_2CrO_4$. Barium and strontium salts of the acid corresponding to CrO_2 were not prepared until 1952-53 [21]. The first of these is formed by a very interesting reaction when a mixture of Cr_2O_3 and $Ba(OH)_2$ is heated in a current of nitrogen to about 800°:

$$Cr_2O_3 + 4Ba(OH)_2 \rightarrow 2Ba_2CrO_4 + H_2 + 3H_2O.$$

It is interesting also that the strontium salt is not formed under similar conditions; it was prepared in a current of nitrogen in accordance with the reaction:

$$SrCrO_4 + Cr_2O_3 + 5Sr(OH)_2 \rightarrow 3Sr_2CrO_4 + 5H_2O.$$

Both salts are microcrystalline green powders. The quadrivalency of the chromium present was confirmed by X-ray and magnetic investigation. It follows from the above discussion that the existence of chromium at a degree of oxidation of +4 is fairly firmly established.

The evidence for the existence of a degree of oxidation of +5 for chromium is equally convincing. Red salts of the type $M_3[CrOCl_5]$ were prepared as early as 1905-1907 [28] by the partial reduction of chromium trioxide in presence of KCl, RbCl, CsCl, or NH_4Cl, with very concentrated hydrochloric acid under cooling, and

it was shown that the cesium salt gives mixed crystals with the analogous red salt of niobium, $Cs_2[NbOCl_5]$. In 1951 [29] pale-purple $K[CrOF_4]$ was prepared by reaction between $K_2Cr_2O_7$ and BrF_3, and the analogous silver salt was prepared also. Magnetic investigation [30] showed that chromium is quinquevalent also in the red perchromates of general formula M_3CrO_8 (M is a univalent metal), which were first prepared by Spitalsky [31]. The formation of traces of the highly volatile fiery-red CrF_5 has been observed both during the fluorination of chromium trifluoride [23] and in the thermal decomposition of $K_2[CrF_6]$ [25], but large amounts of this compound have not yet been prepared. Dark-brown Cr_2O_5 is apparently formed as an intermediate product in the thermal decomposition of chromium trioxide [32], but it has not yet been isolated. On the other hand, the corresponding barium and strontium salts were prepared in 1952 [21] as indicated:

$$4MCrO_4 + 2M(OH)_2 \rightarrow 2M_3(CrO_4)_2 + O_2 + 2H_2O.$$

the reactants being melted together at about 800° in a current of nitrogen. These compounds are finely crystalline blue-black powders, insoluble in water, and readily decomposed by acids with formation of ter- and sexa-valent chromium compounds. X-Ray and magnetic studies of the barium salt confirmed the presence of quinquevalent chromium [21].

As recent investigations have shown, under certain conditions a degree of oxidation of +5 is fairly characteristic for manganese. Although the first relevant compound – the green salt $Ba_3(MnO_4)_2.H_2O$ – was described as early as 1904 [33], this investigation and many others of that period were forgotten so completely that there is no mention at all of a degree of oxidation of +5 for manganese in such well known monographs and textbooks as the books of Sidgwick [34] and Remy [35]. Interest in these compounds was revived only in 1946 [36], when blue crystals of composition $Na_3MnO_4 \cdot 10H_2O$ were prepared. This substance, which was found to give solid solutions with Na_3PO_4, Na_3AsO_4, and Na_3VO_4, was prepared by the reaction of MnO_2 and Na_2O_2 in molten sodium nitrate at 500° and crystallization of the product from concentrated caustic soda solution. The presence of quinquevalent manganese in this substance was later confirmed by a study of its magnetic properties [37]. The compound is decomposed by water as follows:

$$2Na_3MnO_4 + 2H_2O \rightarrow MnO_2 + Na_2MnO_4 + 4NaOH$$

and it has some measure of stability only in cold strongly alkaline solution, in which the above reaction probably becomes appreciably reversible [36]. It was shown in 1952-53 [21] that the anhydrous dark-green salts K_3MnO_4, Na_3MnO_4, $Ba_3(MnO_4)_2$, $Sr_3(MnO_4)_2$ may be prepared also from manganates (by heating them strongly with alkalis in a current of nitrogen) and from manganese dioxide (by heating it fairly strongly with alkalis in a current of oxygen). In 1954 bluish-green Li_3MnO_4 was prepared by the reaction of $LiMnO_4$ with LiOH at 125° in a current of oxygen, and detailed studies were made of the corresponding sodium and potassium salts [38]. It should be noted, however, that attempts to prepare fluorine derivatives of quinquevalent manganese have not been successful [25].

Unlike chromium and manganese, iron has not yet been found at a degree of oxidation of +5. The most promising direction in which syntheses of such compounds might be sought lies in the cautious heating of a ferrate with a very concentrated solution of alkali, when reaction might be expected in accordance with an equation such as:

$$4Na_2FeO_4 + 4NaOH \rightarrow 4Na_3FeO_4 + O_2 + 2H_2O.$$

If such a process can indeed be realized, then the main difficulty will be the establishment of sufficiently mild conditions so that reduction of the iron will not go too far.

The comparatively small amount of material that we have examined here already shows that the study of the unusual degrees of oxidation of the elements gives results of interest and importance from the purely scientific point of view. In some cases these results are also acquiring importance in applied science. A good example is univalent aluminum (the compounds of which were reviewed recently [39]), which is beginning to play a substantial part in the development of a more rational procedure for the smelting of this metal [40]. We may expect that work on the unusual degrees of oxidation of various elements will be further intensified in the near future.

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POSSIBLE MECHANISM OF THE CATALYTIC OXIDATION OF HYDROGEN ON METALS

O.V. Krylov and S.Z. Roginsky

The oxidation of hydrogen is actively catalyzed by the noble metals – platinum, palladium, ruthenium, and others – and also by some non-noble transitional metals (in the elementary state), namely, nickel, iron, copper, molybdenum, and tungsten. Various investigators who have studied this reaction have noted that the noble metals (platinum, palladium, osmium, iridium, ruthenium, and rhodium) are hundreds or thousands of times as active as the non-noble metals [1,2]. The quantitative investigation of oxidation at the surface of a non-noble metal is rendered difficult by the formation of oxide films. It was shown in the earlier investigations of 1920-30 [1,3-6] that the oxide films formed as distinct phases on non-noble metals are considerably less active in this reaction than the metals themselves. When oxygen acts upon noble metals, it undergoes chemisorption without the formation of oxide phases. However, under certain conditions of catalytic reaction the possibility of the formation of oxides at the surface of a noble metal cannot be excluded [7].

The principal kinetic laws governing the oxidation of hydrogen over platinum are as follows: 1) inactive platinum is activated by oxygen or a mixture of hydrogen and oxygen with the result that a constant, stable level of activity is attained [8-14]; 2) over wide ranges of temperatures and pressures (from −100° to +200° and from 0.01 mm to 5 mm) the rate of reaction is directly proportional to the pressure of oxygen and inversely proportional to the square root of the pressure of hydrogen [8-11]:

$$-\frac{dp}{dt} = k\frac{p_{O_2}}{\sqrt{p_{H_2}}} \qquad (1)$$

3) at pressures close to that of the atmosphere the rate of the reaction is proportional to the oxygen pressure and is almost independent of the hydrogen pressure [2,13]; 4) at temperatures above 200° the reaction may pass from the surface to the gas space [15-17], the limiting temperature being raised by reduction in pressure; 5) chemisorbed oxygen does not react appreciably with hydrogen present in the gas space at low temperatures [9,18,19], but with rise in temperature this reaction becomes appreciable; 6) adsorbed hydrogen reversibly poisons the active centers of the platinum, but in presence of the reaction mixture the poisoning rapidly disappears after a period of induction [9,10].

The behavior of the noble metals is essentially similar. This similarity in the kinetics and other features of the catalytic reaction in presence of different noble metals suggests that the mechanism is the same in each case. We have made a detailed investigation of the mechanism for the case of platinum [7-9]. This case is particularly interesting, for experiment shows that platinum behaves the same in the mass, when supported by a carrier, and in the form of a thin film [8].

In examining the mechanism of the oxidation of hydrogen over platinum, we shall start from the already established fact that the absorption of oxygen is an essential condition for the creation of a highly active surface on the noble metal [9]. The relationship of the catalytic activity of the platinum to its oxygen content is approximately linear when the oxygen content is not too high. The activating effect of a detonating hydrogen-oxygen mixture is also due essentially to the absorption of oxygen by the metal [7].

We assume, as our main postulate, that the chief obstacle to the reaction of oxygen with hydrogen is the readiness with which the oxygen passes into an inactive state – powerful sorption, resulting, in the case of non-noble metals, to the formation of phase oxides by the mechanism established by Wagner [20], Mott [21], and others. In the case of the noble metals, we shall identify this inactive state with powerful high-temperature

sorption of oxygen. The oxygen that enters into this surface compound is firmly attached to the metal and, although not reduced by hydrogen, it activates the metal with respect to the oxidation of hydrogen.

Some investigators [22-24], on the basis of data on the work required for the escape of an electron from platinum covered with oxygen, consider that the adsorbed oxygen occurs on the platinum surface in the form of atom ions O^- or O^{--}. There are some indirect data that support the formation of O_3^-. In any case, the various authors all consider that the absorbed oxygen is negatively charged. It is natural to assume that the 6s electrons of the platinum, which are the main source of its electrical conductivity, take part in the formation of these ions — O^-, O^{--}, or O_3^- — on the platinum surface. The capture of some of the s electrons should result in the freeing of some of the d electrons, so that some free places will appear in the d zone of platinum. As early as 1934 [25], one of the present authors emphasized the part played by d electrons in catalysis.

According to our results and those of others [9, 12, 19], at ordinary temperatures the adsorption of hydrogen by platinum in the mass is inappreciable. On dispersed platinum supported by a carrier, the adsorption of hydrogen is appreciable and has an activated character [26]. This view is supported by the results of a study of the effect of hydrogen on the work required for the escape of an electron from the platinum surface [27]. Taking these features of the adsorption of oxygen and hydrogen on the metal into account, we may offer some explanations of the kinetic equations that we have found:

1. When only oxygen enters the transitional complex, the kinetic equation is of the form:

$$W = k_{H_2} \cdot [O_2], \tag{2}$$

in which k depends on $[H_2]$ owing to the poisoning effect of hydrogen. The relationship expressed by Equation 1 may represent the poisoning of the active part of the metal surface, which consists of sites having identical properties, the poisoning agent — hydrogen — being dissociated during adsorption into atoms (Variant 1a). The number of active centers free for reaction with O_2 is

$$N_{act.\,free} = \frac{N_1\,act}{1 + ap^{1/2}}. \tag{3}$$

In which a is a constant and p is the gas pressure. When $ap^{1/2} \gg 1$, we obtain the relationship required*.

A similar result is obtained for a nonuniform surface with the aid of the statistical theory of poisoning [28, 29] (Variant 1b). In this case the physical meaning of the power to which p is raised is different, and this index may be less or greater than 0.5. The limits of error within which it may be determined from our data are ± 0.1. From the point of view of the usual concepts, the model of the nonuniform surface is used in both cases, but in the first variant the distribution of active sites is of a discrete character, and in the second variant it is of an extensive character.

2. The composition postulated for the activated complex is not the only one possible. The only essential feature is the entry of an undissociated oxygen molecule or oxygen ion into the complex. One could assume, for example, that absorbed hydrogen atoms entered into the transitional complex, their concentration being proportional to $[H_2]^{1/2}$ and the poisoning activity proportional to $[H_2]^{-m}$. In the case of a homogeneous surface (with respect to active centers), the retardant must be the undissociated hydrogen molecule, which does not appear very probable (Variant 2a). In the case of a nonuniform surface (Variant 2b), it must be assumed that $[H_2]$ enters into the denominator raised to a fractional power m not differing greatly from unity:

$$W = k_0 \frac{N_1}{[H_2]^m} \cdot [O_2]\,[H_2]^{1/2}. \tag{4}$$

It does not appear to be possible at present to make a final choice between Variants 1a, 1b, and 2b. An answer to this question might be provided by experiments on the oxidation of hydrogen in which hydrogen and oxygen isotopes would be employed. If the transitional complex does not contain hydrogen, then there should be no kinetic isotope effect when H_2 is replaced by D_2 or T_2, but there should be an appreciable kinetic effect in passing from $O_2^{16} + O_2^{18}$ to $O^{16}O^{18}$. The old results of Tuchloski [17] on the effect of the replacement of H_2 by D_2 on the reaction rate over Pd are not altogether unequivocal. Until more accurate data are available, both possibilities must be considered.

*In this case a includes not only the usual adsorption coefficient $a = a_0 e^{+\alpha Q}$, but also the factor K_{diss}.

On the basis of all these considerations, the first stages of the oxidation of hydrogen over platinum, including also the activation process, are very probably as follows:

1) Activation of platinum by oxygen (irreversible):

$$Pt + \tfrac{1}{2} O_2 \rightarrow Pt(O) \equiv Pt^{(O)}.$$

2) Adsorption of hydrogen on active centers (possibly with the formation of ions):

$$Pt^{(O)} + \tfrac{1}{2} H_2 \rightleftharpoons Pt \pm (O) \ldots H^{\pm}.$$

3) Activation of oxygen – the initial stage of the actual catalytic reaction, and probably the limiting stage:

$$Pt^{(O)} + O_2 \rightarrow Pt \pm (O) \ldots O_2^{-}.$$

In order to elucidate the further stages it is essential to carry out special investigations. The schemes suggested below are hypothetical and may be modified considerably in detail in the future; their common feature is the participation of charged particles* in the process and the occurrence of direct electron transitions. Several investigators have recently emphasized the importance of the part played by ionic mechanisms in catalysis [24, 30]. The possibility of ionic mechanisms for the oxidation of hydrogen over platinum follows from data on the kinetics of the oxidation of hydrogen over platinum in a solution [31, 32] and from the operation of similar laws of reaction in the decomposition of hydrogen peroxide [33].

We will write down some non-chain stages of the process:

$$4)\ O_{2\,ads}^{-} + H_2 \rightarrow O_{ads}^{-} + H_2O;$$

$$5)\ O_{ads}^{-} + H_2 \rightarrow H_2O$$

Other variants are:

$$4a \rightsquigarrow 5a)\ O_{2\,ads}^{-} + H_2 \rightarrow H_2O_2 \rightarrow H_2O + {}^1\!/_2 O_2;$$

$$4b \rightsquigarrow 5b)\ O_{2\,ads}^{-} + H \rightarrow HO_{2\,ads}^{-} \xrightarrow{+H} H_2O + O_{ads}^{-};$$

$$4c \rightsquigarrow 5c)\ O_{ads}^{-} + H \rightarrow OH_{ads}^{-} \xrightarrow{+H^+} H_2O.$$

Ionic mechanisms permit also surface chain formation, for example:

$$4d)\ O_{2\,ads}^{-} + H_2 \rightarrow O_{ads}^{-} + H_2O;$$

$$O_{ads}^{-} + O_2 \rightarrow O_{3\,ads}^{-};$$

$$O_{3\,ads}^{-} + H_2 \rightarrow O_{2\,ads}^{-} + H_2O.$$

$$4e)\ O_{2\,ads}^{-} + H \rightarrow HO_{2\,ads}^{-} \xrightarrow{+H_2} H_2O + OH_{ads}^{-} \text{ etc.}$$

Moreover, radicals may be formed and may initiate a homogeneous chain reaction (reaction in the gas space):

$$O_{2\,ads}^{-} + H_2 \rightarrow OH_{ads}^{-} + OH;$$

$$O_{ads}^{-} + H_2 \rightarrow H_{ads}^{-} + OH;$$

$$O_{2\,ads}^{-} + H \rightarrow HO_{2\,ads}^{-} \rightarrow HO_2;$$

$$O_{3\,ads}^{-} \rightarrow O_3 \text{ etc.}$$

It is probable that these considerations will be valid for other noble metals.

SUMMARY

1. An examination is made of the principal results of the study of the kinetics of the oxidation of hydro-

*The "ions" featuring in these schemes are not analogous to the ions in solutions and are probably highly polarized states of molecules and atoms.

gen in presence of platinum.

2. On the basis of a very large amount of experimental material, it is suggested that the stage limiting the process of the oxidation of hydrogen over platinum is the adsorption of oxygen without breakdown of the molecules into atoms.

3. The oxygen that forms a stable surface compound with platinum is not reduced by hydrogen, but it activates the platinum with respect to the reaction of hydrogen oxidation.

4. Suggestions are made concerning the further stages in the process of the oxidation of hydrogen over platinum.

5. The laws governing the oxidation of hydrogen over platinum apply also to palladium and other noble metals, and this fact makes it probable that the mechanism is the same in each case. Some stages of the mechanism that we have analyzed are probably to be found also in the case of the non-noble transitional metals.

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INVESTIGATION OF THE ADSORPTION OF VAPORS ON QUARTZ

COMMUNICATION 2. ADSORPTION ISOTHERMS OF VARIOUS VAPORS

A.I. Sarakhov

With the aid of the apparatus described in the first communication [1] we have investigated the adsorption on highly dispersed crystalline quartz of some polar vapors – water, methanol, and 1,2-dichloroethane at 20° – and some nonpolar vapors – heptane at 20° and 40° and benzene at 20° and 25°.

The quartz was obtained from A.V. Kiselev's laboratory (Moscow State University). Its specific surface, determined from the adsorption isotherm for nitrogen at its boiling point, was 0.6 sq.m/g. X-ray analysis of this adsorbent showed that it was α-quartz having a particle size of about 0.001 cm, which, on the assumption that the particles were spherical, corresponded to a geometric surface of about 0.4 sq.m/g. The quartz was heated at 380° in a vacuum before each series of measurements.

TABLE 1

Adsorption of Water Vapor on Quartz at 20°

(a - adsorption in micromoles per gram; p/p_s - relative pressure, the value of p_s being 17.53 mm; the asterisks indicate desorption points)

a	$p/p_s \cdot 10^3$	a	$p/p_s \cdot 10^3$	a	$p/p_s \cdot 10^3$
0.093	0.00019	3.57	2.68	11.10	58.5
0.243	0.00063	3.91	3.76	11.33*	33.5
0.429	0.00274	4.43	5.82	13.18	70.2
0.672	0.00707	4.82	7.64	13.71*	57.5
0.877	0.0200	5.40	11.2	15.84	79.2
1.157	0.0530	6.03	15.8	20.04*	82.6
1.512	0.149	6.76	21.7	22.35	88.2
2.11	0.451	7.31	28.0	40.65	92.1
2.63	1.018	8.29	37.1		
3.01	1.65	9.22	45.6		

The results of the investigation are given in Tables 1-5 and are represented graphically in Fig. 1. As will be seen from Fig. 1, all of the isotherms are S-shaped, i.e. correspond to the second type of isotherms in Brunauer's classification. The adsorption isotherms for water and methanol vapors are irreversible for the desorption points (not shown in Fig. 1) do not coincide with the adsorption points at relative pressures of 0.8 and less, and at $p/p_s = 0$ an appreciable amount of adsorbed substance remains on the adsorbent. It is probable that in these cases not only physical adsorption occurs, but also chemisorption. The remaining isotherms are completely reversible over the whole of the p/p_s range investigated. The convexity of the isotherms in the region of unimolecular adsorption may be explained partially by some nonuniformity in the adsorbent (edges, apexes, and cracks) and partially by the repulsive forces between molecules of the adsorbed substance, which can exist only if the molecules are all oriented in the same way in the adsorption layer. In all of the adsorption isotherms, except that of water, the formation of a second layer becomes complete at a comparatively high relative pressure (about 0.75). This indicates that the adsorbed molecules of the first layer almost completely screen the field of the adsorbent, so that further adsorption approximates to ordinary condensation in character. This view is confirmed by the fact that in this region the heats of adsorption are approximately the same as the heats of condensation [2]. The steeper rise of the water isotherm and the completion of the second layer at a lower value of p/p_s is probably due to hydrogen bonding between the adsorbed molecules and the occurrence of a considerable amount of adsorption under the action of chemical forces. The sharp rises in the isotherms at relative pressures of greater than 0.8 may be explained by multimolecular adsorption and, at very high values of p/p_s, by capillary condensation at the points of contact between crystals.

TABLE 2

Adsorption of Methanol Vapor on Quartz at 20° (p_s = 93.86 mm)

a	$p/p_s \cdot 10^3$	a	$p/p_s \cdot 10^3$	a	$p/p_s \cdot 10^3$
0.619	0.00300	3.23	9.31	4.84	46.8
0.976	0.0124	3.25°	6.75	4.86	43.2
1.355	0.0466	3.40°	11.85	5.48	57.0
1.600	0.107	3.46	13.2	6.12	65.3
1.893	0.191	3.77°	16.9	6.78	72.9
2.08	0.307	3.78	20.0	7.54	79.5
2.55	0.969	3.83°	17.4	9.40	88.4
2.72	1.86	3.84°	23.1	13.02	95.1
2.87	3.29	4.14°	27.5	18.30	99.4
2.99	4.06	4.14	29.3		
3.11	6.79	4.45	37.4		

TABLE 3

Adsorption of 1,2-Dichloroethane Vapor on Quartz at 20° (p_s = 63.37 mm)

a	$p/p_s \cdot 10^2$	a	$p/p_s \cdot 10^2$	a	$p/p_s \cdot 10^2$
0.057	0.163	1.25	6.30	3.31	53.8
0.092	0.215	1.39	8.30	3.48	58.5
0.155	0.306	1.56	10.97	3.63°	62.0
0.285	0.720	1.75	14.0	3.74	64.1
0.380	0.988	2.10	20.0	4.16	72.2
0.600°	1.37	2.32	24.4	4.65	77.5
0.534	1.51	2.54	30.9	5.47	83.1
0.699	2.16	2.78	37.6	7.18	88.1
0.775	2.29	2.94°	41.2	9.77	91.6
0.975	3.49	2.99	44.2	13.33	95.4
1.122	4.75	3.15°	48.6	20.71	98.2

There are numerous adsorption-isotherm equations in the literature, both empirical equations, and also equations based on various theoretical concepts. We attempted to apply some of these equations to our results. Very often, in the treatment of experimental data on adsorption, use is made of Harkins and Jura's equation [3], which is based on the analogy between the behavior of monolayers of macromolecular substances on water and that of adsorbed layers on a solid:

$$\log \frac{p}{p_s} = B - \frac{A}{a^2}, \quad (1)$$

in which B and A are constants, a is the adsorption, and p/p_s is the relative pressure. When experimental data are in accord with this equation, a plot of $1/a^2$ against $\log p/p_s$ should be a straight line, the slope of which is a function of the specific surface of the adsorbent: $s = k\sqrt{A}$, in which k is a coefficient dependent on the properties of the adsorbed substance, but not dependent on the properties of the adsorbent. Equation 1 describes our isotherms satisfactorily in the region of unimolecular coverage. However, experiment indicates that the value of k does depend on the adsorbent. Using the value of the specific surface of quartz found from the adsorption isotherm for nitrogen, we found that for quartz the adsorption of methanol is characterized by k = 0.164 sq. m per micromole, whereas for barium sulfate [4] k = 0.068 sq.m. per micromole, i.e., there is more than a twofold variation in k from one adsorbent to another.

TABLE 4

Adsorption of Heptane Vapor on Quartz ($p_{s20°}$ = 35.42 mm; $p_{s40°}$ = 92.366 mm)

Temp. °C	a	$p/p_s \cdot 10^3$	a	$p/p_s \cdot 10^3$	a	$p/p_s \cdot 10^3$
20	0.025	0.00114	0.583	4.15	2.82	68.7
	0.144	0.00205	0.675	5.53	3.45	77.6
	0.151	0.0101	0.737	7.27	4.42°	84.5
	0.163	0.0359	0.765°	6.97	4.60	87.1
	0.185	0.0943	0.918	11.57	4.76	87.1
	0.227	0.229	1.26	22.5	4.94	88.0
	0.277	0.481	1.53	32.0	6.44	92.3
	0.307	0.683	1.79	41.6	7.65	94.3
	0.375	1.191	2.12	52.7	9.86	96.6
	0.459	2.09	2.81°	67.9	16.20	98.8
40	0.159	0.0140	0.332	1.007	1.00	19.3
	0.169	0.0410	0.396	1.88	1.21	28.5
	0.194	0.090	0.483	3.29	1.35	32.3
	0.228	0.189	0.533	4.35	1.68	43.5
	0.268	0.466	0.723	9.97		
	0.308	0.790	0.878	15.04		

Brunauer, Emmett, and Teller's equation [5], which is generally used for the determination of the specific surfaces of adsorbents, also describes our isotherms satisfactorily, but the range of its applicability is somewhat narrower than usual.

TABLE 5

Adsorption of Benzene Vapor on Quartz ($P_{t20°}$ = 75.20 mm; $P_{t25°}$ = 95.15 mm)

Temp. °C	a	$p/p_t \cdot 10^3$	a	$p/p_t \cdot 10^3$	a	$p/p_t \cdot 10^3$
20	0.222	0.32	2.83*	44.7	5.00	81.0
	0.275	0.46	2.79	44.8	5.80	85.1
	0.416	1.24	3.00*	50.2	6.25	86.6
	0.630	2.72	3.10	54.7	7.23	90.5
	0.773	4.20	3.34*	59.7	7.81	92.1
	1.078	7.44	3.39	60.6	8.71	93.2
	1.475	12.36	3.45	62.3	8.92	93.7
	1.772	17.1	3.57	65.0	9.72	94.9
	2.047*	22.5	3.68	67.5	10.44	95.7
	2.114	24.4	3.82	69.3	11.65	96.9
	2.133	24.7	4.29	74.9	13.88	98.1
	2.316	29.9	4.48	76.8	15.52	99.3
	2.518	36.3	4.91	80.5		
25	0.008	0.036	0.553	2.57	2.81*	50.7
	0.025	0.059	0.696	4.10	3.07	58.2
	0.057	0.078	0.736	4.31	3.18*	60.1
	0.076	0.104	0.898	6.16	3.40	63.2
	0.093	0.118	0.965	7.31	3.45	65.9
	0.111	0.139	1.211	10.30	3.79	72.3
	0.130	0.175	1.27	10.9	3.83	72.4
	0.174	0.291	1.42	13.2	4.18	76.2
	0.295	0.576	1.77	19.3	4.66	80.1
	0.349	1.04	1.77*	20.5	5.25	83.9
	0.354	1.09	2.03	27.1	6.08	87.7
	0.496*	1.84	2.21	32.0		
	0.489	1.09	2.40	38.3		
	0.546*	2.39	2.60	44.7		

TABLE 6

Thicknesses of Adsorbed Films at High Saturations

Adsorbed substance	Number of layers when		Maximum value obtained	
	p/p_s = 0.8	p/p_s = 0.9	p/p_s	No. of layers
Water	2.8	5.2	0.921	7.5
Methanol	2.5	3.3	0.994	6.0
Benzene	2.6	4.0	0.968	7.5
Heptane	3.1	4.6	0.988	13.4
1,2-Dichloroethane	2.4	4.0	0.982	10.0

Adsorption measurements on heptane and benzene at two different temperatures provided data for the calculation of differential heats of adsorption from the equation

$$Q_d = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_a \qquad (2)$$

The relationship between the differential heat of adsorption and the extent of adsorption is shown for benzene and heptane in Fig. 2. Each curve has a clearly defined maximum in the region of a complete unimolecular layer ($\Theta \approx 1$, Θ being the fractional unimolecular coverage), this being indicated on the curve by a_m. When adsorption increases beyond the unimolecular stage, the differential heat falls and approximates to the heat of condensation. The different courses taken by the curves in the unimolecular region indicate a substantial difference in the processes accompanying the sorption of these vapors. The fall in the differential heats of adsorption of benzene may result, firstly, from a certain nonuniformity of the quartz surface and, secondly, from the appreciable polarization of benzene in the adsorbed state, so that repulsive forces arise between the molecules, which are identically oriented induced dipoles. This view is indirectly confirmed by the definite solubility of benzene in water and therefore also the appreciable interaction of benzene molecules with the OH groups that cover the quartz surface. With further increase in the extent of adsorption, the distances between benzene molecules are reduced and short-range attractive forces begin to predominate. In this case the maximum on the differential heat curve should be at $\Theta = 1$. However, before the unimolecular layer is complete, some adsorption in the second layer apparently occurs. As the heat of adsorption in the second layer is less than that in the first owing to screening of the field of the adsorbent, the maximum on the curve $Q = f(a)$ is displaced to the left from the point a_m, a behavior that will be noted on both curves. Heptane, having an insignificant solubility in water, evidently forms considerably weaker bonds with water and therefore with the OH groups covering quartz than benzene does. Hence, at low adsorption

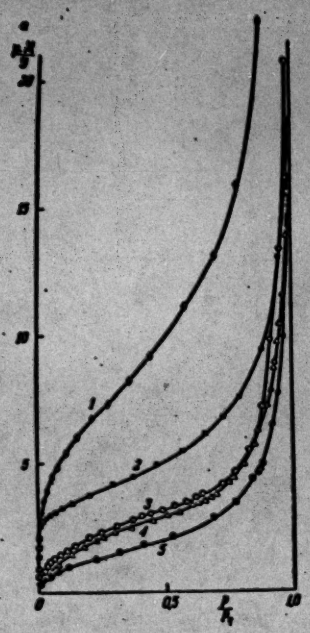

Fig. 1. Adsorption isotherms for vapors: 1) water; 2) methanol; 3) 1,2-dichloroethane; 4) benzene; 5) heptane (20° on quartz).

coverage the heat of adsorption may be less than the heat of condensation. The increase in the heat of adsorption, continuing until a unimolecular layer is completed, may be explained, as in the case of benzene, by an increase in the effect of attractive forces between adsorbed molecules as their concentration in the adsorbed layer increases. However, since the heptane molecule is nonpolar and is apparently not appreciably polarized in the adsorption field of the quartz surface, no repulsive forces arise between these molecules. It may be supposed that, in the adsorption of heptane on quartz, the first molecules adsorbed play the part of adsorption centers that are somewhat more active than the quartz surface itself.

The occurrence of maxima on Q = f(a) curves at θ = 1 has been observed by many investigators: by Orr [6] in a study of the adsorption of nitrogen and argon on crystals of potassium and cesium chlorides; by Rhodin [7] in an investigation of the adsorption of nitrogen and argon on monocrystals of copper and on a zinc surface; by Beebe and coworkers [8] in the course of direct measurements of the heats of adsorption of nitrogen and argon vapors on Graphon carbon black, distinct maxima at θ = 1 and θ = 2 being observed; and by Bering and Serpinsky [9] in an investigation of the adsorption of nitrogen vapor on sodium chloride crystals. The view that we have taken regarding the maxima on Q = f(a) curves is the same as that taken in the literature cited above. It must be stated that in our case the results of the calculation of differential heats of adsorption must be treated with some caution, since the temperature interval between the isotherms, especially the

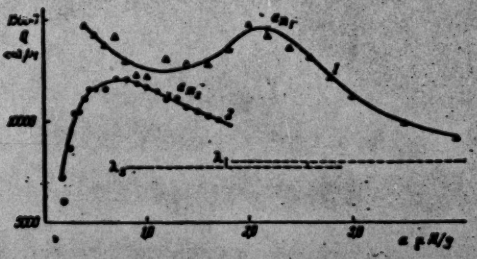

Fig. 2. Differential heats of adsorption: 1) benzene; 2) heptane (on quartz).

benzene isotherms (5°), is not large enough to yield reliable data. This is particularly true for the region of low coverage.

The region of high adsorption is of no less interest. In particular, many researchers report the formation of very thick layers of adsorbed substance (up to 100 molecular layers and up to 1000 A) in the region of saturation [10-15]. Some theoretical papers have appeared [16-18] in which attempts are made to explain the formation of such thick adsorbed layers. On the other hand there have been investigations [19] in which no such formation of thick layers was observed. Using the value of a_m (extent of adsorption corresponding to the completion of a unimolecular layer) calculated by Brunauer, Emmett, and Teller's method, we

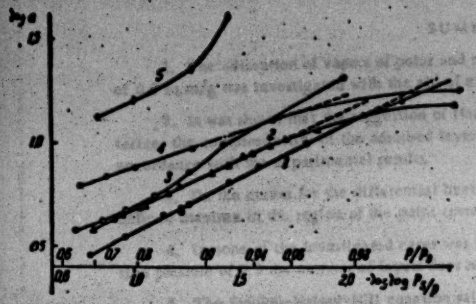

Fig. 3. Verification of the applicability of the equation for the multimolecular adsorption of vapors: 1) heptane; 2) benzene; 3) 1,2-dichloroethane; 4) methanol; 5) water (on quartz).

determined the number of layers formed in the adsorption of various substances on quartz (Table 6). It will be seen that in the region of saturation very thick adsorbed layers are not formed. It should be noted that these results, if incorrect, can only be too high, since it is assumed in the calculation that there is no capillary condensation at the places of contact between the particles.

Among theoretical papers devoted to the multimolecular region of adsorption, those of Halsey [20], Hill [21], and McMillan and Teller [22] deserve attention; they lead to the adsorption equation:

$$\ln \frac{p_s}{p} = \frac{k}{v^s} \qquad (3)$$

in which v is the number of adsorbed layers at pressure p; p_s is the saturated vapor pressure; and k is a proportionality constant determined by molecular forces. Halsey proposed a more general form of this equation, in which the power index 3 is replaced by the more general s. The physical basis of Equation 3 lies in the assumption that the potential of van der Waals forces between adsorbed atoms and the adsorbent falls off inversely as the cube of the distance. Experimental data obtained by Harkins and Jura [23] for the adsorption of nitrogen vapor on anatase (TiO_2 powder) are closely described by Equation 3 with a power index of 2.67 instead of 3. According to Drain and Morrison [24], $s = 2$ for the adsorption of argon on rutile. In a study of the adsorption of nitrogen, argon, and oxygen on aluminum foil, Bowers [25] obtained close accord with Equation 3 with a power index of approximately 3. We have verified the applicability of the equation of Frenkel, Halsey, and Hill to our data, but instead of the number of adsorbed layers we took the value of the adsorption, since in this way we could avoid the use of an uncertain value for the density of the substance in the adsorbed state, uncertain values for the surface of the adsorbent and for a_m, and the insufficiently valid assumption of the regular formation of layers of adsorbed substance on the adsorbent. When this is done, Equation 3 must be regarded rather as a semi-empirical equation than as a theoretical equation of the Frenkel-Halsey-Hill type.

Taking logarithms in Equation 3, we obtain a linear relationship between $\log \log p_s/p$ and $\log a$:

$$\log \log \frac{p_s}{p} = \log k - s \log a. \qquad (4)$$

Fig. 3 shows our experimental data expressed in these coordinates. It will be seen that the adsorption isotherms of heptane, benzene, and methanol are straight lines, so that Equation 4 is applicable. The applicability of the equation is somewhat less for 1,2-dichloroethane, and it is not applicable at all for water. It may be supposed that, in the case of water, the occurrence of hydrogen bonding results in the nonapplicability of Equation 4, and therefore also of Equation 3. The power index s calculated from the graph (Fig. 3) differs from 3 in all cases; for heptane it is 1.90, for benzene 2.06, for methanol 2.88, and for 1,2-dichloroethane 1.69, behavior that is in accord with the investigation of Bowers [26], who studied the thickness of saturated helium films on aluminum and obtained $s = 2.0 \pm 0.3$, and with those of Bering [27], who obtained $s = 2$ for the adsorption of methanol vapor on a mercury surface.

It is thus shown that Equation 4 is applicable in the region of multimolecular adsorption on nonporous adsorbents in the range of relative pressures of 0.65-0.97.

In conclusion I wish to express my deep indebtedness to M.M. Dubinin, B.P. Bering, and V.V. Serpinsky for their constant interest in this investigation.

SUMMARY

1. The adsorption of vapors of polar and nonpolar substances on crystalline quartz having a specific surface of 0.6 sq.m/g was investigated with the aid of a highly sensitive adsorption balance.

2. It was shown that the suggestion of Harkins and Jura to the effect that the coefficient k - which characterizes the compressibility of the adsorbed layer - is independent of the nature of the adsorbent surface is not in accordance with the experimental results.

3. On the curves for the differential heats of adsorption of benzene and heptane vapors, there are clearly defined maxima in the region of the point corresponding to the complete filling of a unimolecular layer.

4. In none of the investigated cases was the formation of a very thick adsorbed film observed. At a relative pressure of 0.9 the number of layers does not exceed 4-5, and at $p/p_s = 0.98$ the number of layers is 6-12.

5. The Frenkel-Halsey-Hill equation satisfactorily describes all of the isotherms (with the exception of that of water) in the middle region of multimolecular adsorption, but the power index must be given values of less than 3.

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*T.p. = C.B. Translation pagination.

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LIQUATION IN THE SYSTEM $ZrO_2 - SiO_2$

N.A. Toropov and F.Ya. Galakhov

The study of the systems containing zirconia is associated with the development of the manufacture of new kinds of silicate products, particularly refractories. The system zirconia-silica is of great importance, not only in itself, but also as the basis for the study of ternary silicate systems.

Zhirnova [1] was the first to determine the fusion diagram, and according to her results zircon $ZrSiO_4$ melts without decomposition and gives two eutectics: one with zirconia and one with silica. The fusion of zircon was described similarly in earlier papers [2], but the description was not confirmed in later investigations [3, 4] according to which zircon melts with decomposition and there is only one eutectic.

These contradictions made it desirable to make a further verification of the character of the fusion of zircon. In the course of this work the phenomenon of liquation was observed in the system, and this caused us to extend the investigation to a larger region of the system.

EXPERIMENTAL

Starting materials: zirconia, obtained by the calcination of zirconium nitrate and containing 0.35% SiO_2, 0.03% TiO_2, 0.16% Al_2O_3, and 0.06% Fe_2O_3, and powdered crystal quartz containing 99.90% SiO_2. Weighed amounts of the materials were mixed carefully in an agate mortar, moistened with a dextrin solution, compressed into the form of rods, and fused in an electric arc. The experiments were carried out in a microfurnace similar to that described previously [5]; the tungsten spiral was made from wire 0.8 mm in diameter, the internal diameter of the spiral was 5 mm, and the number of turns was 20. The spiral was protected by five tantalum screens and one external nickel screen. This arrangement enabled us to heat the samples to 2500° in oxygen-free argon. The temperature was measured with an optical pyrometer. The pyrometer was calibrated by the use of samples having known melting points: Al_2O_3 – 2050°, $MgO \cdot Al_2O_3$ – 2135°, La_2O_3 – 2316° and BeO – 2520°. The melting point was determined by observing the sample through the optical pyrometer, the temperature at which distinct melting occurred being recorded. The time taken in heating the sample from 1500° until it began to melt was 10-20 seconds, and the experiment was repeated three or four times, a new test sample being taken each time. Owing to the volatility of silica at high temperatures, all of the experiments had to be carried out very quickly with a minimum time of treatment.

No maximum for the compound $ZrSiO_4$ was found on the melting point curve. The examination of polished sections of samples differing in composition showed that only one crystalline phase separated, this being very prone to form dendrites or, occasionally, isometric grains (Fig. 1). The refractive index of the crystals, which was found to be greater than 2.05, indicated that they were zirconia. X-ray analysis of the crystals showed that they consisted of a solid solution of ZrO_2 in SiO_2, as found also in previous investigations [1, 3]. After being melted, all of the samples were opaque. In immersion preparations, a transparent glass was observed in samples containing not more than 20% of zirconia. As the zirconia content was increased, the glass became brown and more opalescent, and finally opaque.

Natural zircon crystals were also heated for 10-15 seconds at various temperatures and then examined in the form of polished sections. At 1800° glass and very fine crystals appeared. With rise in temperature the relative amount of glass increased and the dimensions of the newly formed crystals increased. It was found, unexpectedly, that two immiscible liquids were formed. A structure corresponding to this behavior was clearly observed in the sections. One liquid was dispersed in the other in the form of spherical or oval-shaped drops. A

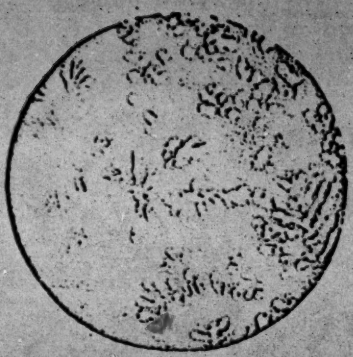

Fig. 1. Zircon crystals (reflected light; magnification 450)

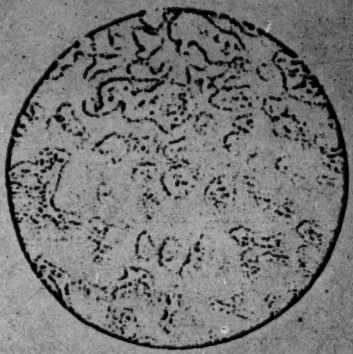

Fig. 2. Liquation in the system $ZrO_2 - SiO_2$ (reflected light; magnification 450)

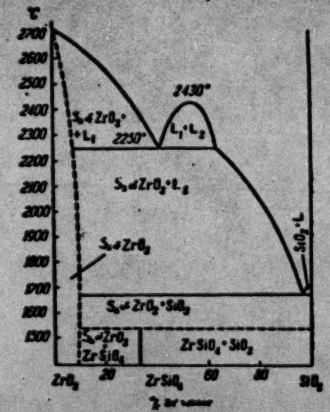

Fig. 3. Phase diagram of the system $ZrO_2 - SiO_2$ (according to the work of the authors and of Curtis and Sowman) S_s = solid solution.

photomicrograph of a section is shown in Fig. 2. The liquid that forms discrete droplets crystallizes, and very fine ZrO_2 crystals separate. The other liquid forms a turbid brown glass. It has thus been established that Barlett's suggestion [6] that two immiscible liquids may be formed in the system is correct. However, Barlett did not carry out any precise investigations in this direction.

Our further experiments had the object of defining the limits of the liquation field. The samples were heated until fully melted, cooled to the annealing temperature, at which they were kept for 5-30 seconds, and then pushed into the cold zone of the furnace with the aid of a magnet. Owing to its small dimensions, the sample cooled rapidly, particularly in the first stage of cooling. In order to determine the extent to which the composition of the sample changed on account of the vaporization of the silica under the experimental conditions, silica contents were determined on an unheated sample and on a sample heated for ten seconds at 2350°. The amount of material necessary for analysis was prepared by carrying out the heat treatment on numerous samples of identical composition. The silica content was determined from the loss in weight resulting from treatment with a mixture of hydrofluoric and sulfuric acids. In view of the fairly high purity of the starting materials, this indirect method for the determination of silica can be regarded as quite satisfactory. The original sample contained 55.60% of silica, and the heated sample also contained 55.60% of silica. The complete identity of the two results is of course fortuitous, but they indicate that silica volatilizes to a quite insignificant extent, this being attributable to the shortness of the period of heating. The products resulting from the heat treatment were examined microscopically in the form of sections. The results of the investigation are presented in the table.

TABLE

Results of the Determination of the Liquation Field in the System $ZrO_2 - SiO_2$

Sample No.	Composition (% by weight)		M.p. (°C)	Annealing temperature (°C)	Phases
	ZrO_2	SiO_2			
3	75	25	2400		
4	67	33	2350	2450	Glass
				2360	ZrO_2 + glass
12	62	38	2280	2400	Glass
				2320	ZrO_2 + glass
5	57	43	2280	2350	Glass
				2300	Two glasses
8	52	48		2450	Glass
				2370	Two glasses
				2280	" "
				2240	ZrO_2 + glass
6	47	53		2420	Glass
				2420	Two glasses
				2400	" "
				2320	" "
				2200	ZrO_2 + glass
14	43	57	2230	2400	Two glasses
				2350	" "
				2260	ZrO_2 + glass
9	40	60	2260	2350	Glass
				2300	Two glasses
				2200	ZrO_2 + glass
13	35	65	2200	2300	Glass
				2230	ZrO_2 + glass
7	30	70	2180		

Fig. 3 shows the phase diagram for the system $ZrO_2 - SiO_2$. That part of the diagram lying below 1800° is taken completely from Curtis and Sowman's paper [4]. The field of solid solutions was not investigated, and its limits are taken from the same paper. The liquation field is in the section from 41 to 42% by weight of SiO_2 (58.3-76.80 mole-%), and it begins at 2250° and has a critical point at 2430° (53% SiO_2).

In silicate systems the formation of two immiscible liquids has been observed most frequently when certain bivalent cations are present [7]. Liquation in a silicate melt in presence of a cation of higher valency (other than Zr^{4+}) is known only for Ti^{4+} [8]. According to the theoretical concepts developed for silicates by Esin [9], the occurrence of liquation is determined by the force of interaction between the metal cation and O^{2-}, and the greater the energy of interaction, the lower the silica content at which liquation begins. In the series of bivalent cations, with reduction in radius - and therefore with increase in the force of interaction with O^{2-} - the silica content at which liquation of the system begins also diminishes. The most powerful of the bivalent cations is Mg^{2+} (0.78 A). The Zr^{4+} cation, though of greater radius (0.87 A), should interact more strongly with oxygen ions because of its high charge, which is double that of the magnesium ion. Ti^{4+} is a still stronger cation (0.64 A). In the respective binary systems formed with these cations, liquation begins at silica contents of 60, 58.3, and 9.1 mole-% SiO_2. Thus, when we pass from bivalent to quadrivalent cations, we find that the same law holds with respect to the relationship between the strength of the cation and the beginning of liquation in the system.

SUMMARY

1. The system $ZrO_2 - SiO_2$ was investigated at 1800-2500°.
2. It was shown that zircon $ZrSiO_4$ melts with decomposition into zirconia and a liquid.

3. Liquation occurs in the system at high temperatures. The temperatures and concentrations at which the two liquids coexist were determined.

4. The high-temperature region of the phase diagram of the system $ZrO_2 - SiO_2$ was constructed.

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EXCHANGE REACTIONS OF STEREOISOMERIC MERCURY DERIVATIVES OF STILBENE

A.N. Nesmeyanov, A.E. Borisov, and N.A. Volkenau

Continuing our investigation of the stereochemistry of electrophilic and radical exchange, we have now attempted to bring the stereoisomeric mercury derivatives of stilbene described in a previous communication [1] into exchange reaction with heavy-metal salts. It was found that mercury derivatives of stilbene, unlike the corresponding 2-chlorovinyl compounds [2], have little tendency to exchange their mercury atoms for atoms of other metals.

Cis- and trans-bis(1,2-diphenylvinyl)mercurys react with $TlCl_3$ as follows, without yielding organothallium compounds:

$$[C_6H_5CH{=}CC_6H_5]_2Hg + TlCl_3 \rightarrow C_6H_5CH{=}C(C_6H_5)HgCl + C_6H_5CH{=}C(C_6H_5)Cl + TlCl. \quad (1)$$

When treated with tin-sodium alloy, the stereoisomeric 1,2-diphenylvinylmercury chlorides are converted into the corresponding bis(1,2-diphenylvinyl)mercurys. Under severe conditions, trans-1,2-diphenylvinylmercury chloride yields also a little trans-stilbene.

Both in alcohol and also in absence of solvent (in the melt at 240-260°), trans-bis(1,2-diphenylvinyl)mercury fails to react with $SnCl_2$. When treated with $SnCl_2$ in alcohol, trans-1,2-diphenylvinylmercury chloride symmetrizes with formation of trans-bis(1,2-diphenylvinyl)mercury. In acetone both trans-1,2-diphenylvinylmercury chloride and trans-bis(1,2-diphenylvinyl)mercury react with $SnCl_2$ with formation of trans-stilbene, i.e. they react characteristically for organomercury compounds in which the radicals are at the left end of the series of relative electronegativeness [3].

Organotin compounds are obtained only when mercury derivatives of cis-stilbene are treated with $SnCl_2$ in acetone, but even then the reaction is not as smooth as usual [3]. At room temperature one of the products is bis(1,2-diphenylvinyl)tin dichloride, formed by Equation 2 (or 3):

$$[C_6H_5CH{=}CC_6H_5]_2Hg + SnCl_2 \rightarrow [C_6H_5CH{=}CC_6H_5]_2SnCl_2 + Hg \quad (2)$$

or

$$2C_6H_5CH{=}C(C_6H_5)HgCl + 2SnCl_2 \rightarrow [C_6H_5CH{=}CC_6H_5]_2SnCl_2 + SnCl_4 + 2Hg, \quad (3)$$

but this substance could not be isolated in the pure state as it was always mixed with 1,2-diphenylvinyltin trichloride and cis-stilbene. After hydrolysis with aqueous ammonia, however, it was possible to isolate α-stilbenestannonic acid and bis(1,2-diphenylvinyl)tin oxide. The first of these compounds is soluble in ether, chloroform, carbon tetrachloride, and benzene, but insoluble in alcohol and petroleum ether; it melts at 157-160°. The second compound is insoluble in organic solvents and is infusible. When the reaction with $SnCl_2$ is carried out at 70-80°, only 1,2-diphenylvinyltin trichloride (together with 20-30% of cis-stilbene) is formed.

It is probable that the exchange reaction is complicated by disproportionation. The isolation of 1,2-diphenylvinyltin trichloride from its mixture with liquid cis-stilbene is difficult and is accompanied by losses. In most of the experiments, therefore, the organotin trichloride was hydrolyzed to α-stilbenestannonic acid, which was then converted into 1,2-diphenylvinyltin trichloride by the action of $SOCl_2$ [4]. The analogous conversion of bis(1,2-diphenylvinyl)tin oxide into bis(1,2-diphenylvinyl) dichloride was not found to be possible, treatment with $SOCl_2$ resulting in the formation of only 1,2-diphenylvinyltin trichloride, which was obtained in low yield. The organotin compounds so obtained readily exchanged their tin atoms for mercury. Thus, with $HgCl_2$, 1,2-diphenylvinyltin trichloride gives cis-1,2-diphenylvinylmercury chloride, and with HgO α-stilbene-

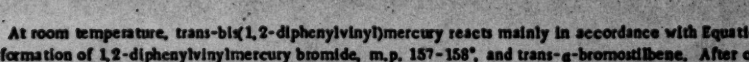
stannonic acid and bis(1,2-diphenylvinyl)tin dichloride give cis-bis(1,2-diphenylvinyl)mercury. In an alcoholic medium, treatment of cis-1,2-diphenylvinylmercury chloride or cis-bis(1,2-diphenylvinyl)mercury with $SnCl_2$ gives cis-stilbene.

Although mercury derivatives of the stereoisomeric stilbenes do not readily exchange mercury for another metal, the transfer of a stilbene residue from one mercury atom to another is effected fairly easily. In the present investigation we have made a detailed study of such reactions. It was found that the desymmetrization of cis- and trans-bis(1,2-diphenylvinyl)mercurys by means of mercuric bromide gives the stereoisomeric 1,2-diphenylvinylmercury bromides, m.p. 118-120° and 157-158° respectively. As agents for the symmetrization of the stereoisomeric 1,2-diphenylvinylmercury halides, Na_2SnO_3 and NiI$_2$ can be used, as well as KI and C_4H_9Li [1].

With the object of investigating the stereochemistry of these reactions, we attempted to reconvert the organometallic compounds into the original α-bromostilbenes. We used dioxane dibromide as reagent [5]. The stereoisomeric mercury derivatives of stilbene were found to react with dioxane dibromide in accordance with Equations 4 and 5:

$$[C_6H_5CH = CC_6H_4]_2Hg + Br_2 \cdot O\langle\rangle O \rightarrow C_6H_5CH = C(C_6H_4)HgBr + $$

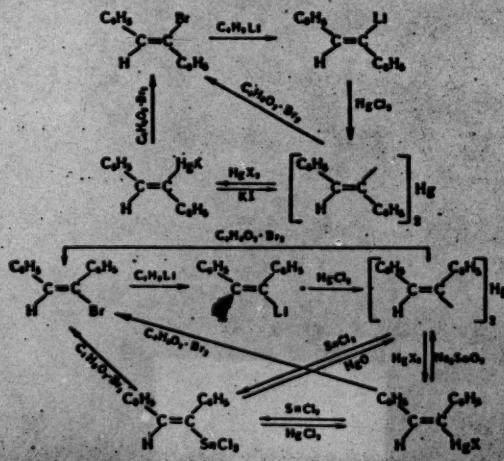
$$+ C_6H_5CH = C(C_6H_4)Br. \qquad (4)$$



$$C_6H_5CH = C(C_6H_4)HgX + Br_2 \cdot O\langle\rangle O \rightarrow C_6H_5CH = C(C_6H_4)Br + HgBrX. \qquad (5)$$

At room temperature, trans-bis(1,2-diphenylvinyl)mercury reacts mainly in accordance with Equation 4, with formation of 1,2-diphenylvinylmercury bromide, m.p. 157-158°, and trans-α-bromostilbene. After one hour at 70-80°, the trans isomers of bis(1,2-diphenylvinyl)mercury and 1,2-diphenylvinylmercury chloride, and also the high-melting 1,2-diphenylvinylmercury bromide, yield only $HgBr_2$ and trans-α-bromostilbene. Free bromine splits trans-bis(1,2-diphenylvinyl)mercury completely at room temperature. The mercury derivatives of cis-stilbene react with dioxane dibromide with formation of cis-α-bromostilbene and $HgBr_2$ already at room temperature. By this method it is possible to synthesize 1,2-diphenylvinylmercury bromide, m.p. 118-120°, only when strictly defined proportions of reactants are used. With dioxane dibromide the above-described 1,2-diphenylvinyltin trichloride, α-stilbenestannonic acid, and bis(1,2-diphenylvinyl)tin oxide yield cis-α-bromostilbene.

The reactions that we have carried out may be represented as follows (see also [1]):



All of these reactions are stereochemically pure, i.e. only one geometric isomer is obtained as product. The configurations of the stereoisomeric α-bromostilbenes are known [6, 7]. It will be seen from the scheme of reactions that, starting from trans-α-bromostilbene, we may carry out closed cycles of reactions consisting of two, three, or four links, and so return to the original trans-α-bromostilbene. Starting from cis-α-bromostilbene, we may carry out cycles having two, three, four, or five links, and again return to cis-α-bromostilbene. It is improbable that in all of these cycles inversion of the configuration occurs the exact number of times necessary for a return to the original form in each case. It is more probable that all of the compounds obtained from trans-α-bromostilbene have trans configurations, and all obtained from cis-α-bromostilbene have cis configurations. This conclusion is in accord with the tentative configurations assigned to the organomercury stereoisomers in a previous investigation [1]. As regards the compounds prepared in the present investigation, this conclusion enables us to assign cis configurations to the 1,2-diphenylvinylmercury bromide of m.p. 118-120°, the 1,2-diphenylvinyltin trichloride of m.p. 108-110°, and the α-stilbenestannonic acid of m.p. 157-160°. The trans configuration can be assigned to the 1,2-diphenylvinylmercury bromide of m.p. 157-158°.

The behavior observed in all of these reactions confirms the correctness of the rule relating to the preservation of geometric configuration in electrophilic and radical exchange reactions [2]. It is difficult to say why mercury derivatives of stilbene have such low reactivities, but it is very probable that the cause is to be found in steric difficulties. This view is confirmed by the fact that styrene derivatives of the type $C_6H_5CH = CHHgX$ [8] readily exchange a mercury atom for tin or thallium.

EXPERIMENTAL

1. Reaction of the Stereoisomeric Bis(1,2-diphenylvinyl)mercurys with Thallium Trichloride. A solution of 2.5 g (0.0080 mole) of $TlCl_3$ in 16.6 ml of ether was added to a solution of 4 g (0.0072 mole) of trans-bis(1,2-diphenylvinyl)mercury in 200 ml of anhydrous dioxane at 80°. The mixture was heated at 70-80° for one hour. The precipitate was then filtered off, washed with ether, and treated with boiling dioxane; it consisted of TlCl and weighed 1.85 g (97%). Suitable treatment of the combined dioxane solutions and repeated recrystallizations from alcohol yielded 2.7 g (91%) of trans-1,2-diphenylvinylmercury chloride, m.p. 140-141° (no depression in a mixture test) and 1.35 g (87%) of trans-α-chlorostilbene, m.p. 62-63.5° (the literature [9] gives 53-54°). Lowering of the reaction temperature resulted in incomplete decomposition of the original substance. The reaction does not go in ether owing to the low solubility of the original substance.

Under the same conditions, cis-bis(1,2-diphenylvinyl)mercury yield: 98% of TlCl and 91% of cis-1,2-diphenylvinylmercury chloride, m.p. 130-131°. In ether the course of the reaction is the same, but it is very slow and incomplete.

2. Reaction of the Stereoisomeric 1,2-Diphenylvinylmercury Chlorides with Tin-Sodium Alloy. a) trans-1,2-Diphenylvinylmercury Chloride. A mixture of 2 g (0.0048 mole) of trans-1,2-diphenylvinylmercury chloride, 6 g of a tin-sodium alloy (15% of sodium), and 20 ml of absolute xylene was boiled for three hours. The precipitate was then filtered off and treated with two portions of boiling xylene. The combined xylene filtrates yielded 1.05 g (77%) of trans-bis(1,2-diphenylvinyl)mercury, m.p. 238-241° after recrystallization from dioxane (no depression in a mixture test), and a very small amount of trans-stilbene, m.p. 122-123° after recrystallization from alcohol (no depression in a mixture test). It was found that, when the reaction was carried out in benzene, an eight-hour boil was necessary in order to attain a 70% yield of trans-bis(1,2-diphenylvinyl)mercury. In this case no trans-stilbene by-product was observed.

b) cis-1,2-Diphenylvinylmercury Chloride. A mixture of 3 g (0.0072 mole) of cis-1,2-diphenylvinylmercury chloride, 9 g of the tin-sodium alloy, and 60 ml of absolute benzene was boiled for three hours. The precipitate was filtered off and treated with two portions of boiling benzene. The combined benzene filtrates yielded 1.95 g (97%) of cis-bis(1,2-diphenylvinyl)mercury, m.p. 144-145° after recrystallization from a mixture of benzene and alcohol (no depression in a mixture test).

3. Reaction of trans-Bis(1,2-diphenylvinyl)mercury and of trans-1,2-Diphenylvinylmercury Chloride with Stannous Chloride. All experiments on the reaction of trans-bis(1,2-diphenylvinyl)mercury and of trans-1,2-diphenylvinylmercury chloride with $SnCl_2$ were carried out in sealed tubes. At the end of the period of heating, the tubes were opened and the precipitate of mercury or unchanged reactant was filtered off. Solvent was completely removed from the filtrate under reduced pressure, and the solid residue was crystallized from absolute alcohol. In those experiments (Nos. 3, 5, and 7 in Table 1) in which a mixture of trans-stilbene and trans-1,2-diphenylvinylmercury chloride was formed, the substance was dissolved in acetone and treated with an acetone solution of KI. The trans-1,2-diphenylvinylmercury chloride was then converted into trans-bis(1,2-diphenyl-

vinyl mercury, which was readily separated owing to its low solubility. Stilbene separated from the solution when acetone was distilled off. The results of the experiments are given in Table 1.

Reaction of trans-bis(1,2-diphenylvinyl) mercury with anhydrous $SnCl_2$ in absence of solvent (in the fused state) was also carried out in a sealed tube. When 1 g (0.0018 mole) of trans-bis(1,2-diphenylvinyl)mercury was heated with 0.5 g (0.0026 mole) of anhydrous stannous chloride at 240-260° for 10-15 minutes, 0.95 of the original substance was recovered unchanged (m.p. 242-243°). When heating was prolonged beyond 15 minutes, decomposition set in with separation of mercury, small amounts of trans-stilbene, and a resinous mass, free from metal.

TABLE 1

Expt. No.	Amount of			Temperature (°C)	Time (hrs)	Yield of trans isomer (g)		
	Mercury compound (g)	$SnCl_2$ (g)	Solvent (ml)			R*H	RHgCl	R_2Hg
			trans-bis(1,2-diphenylvinyl)mercury					
1	0.5	0.25	C_2H_5OH 20	100	9	–	–	0.45
2	0.5	0.25	C_2H_5OH 20	180	8	–	–	0.45
3	1	0.5	C_2H_5OH + HCl gas 30	100	18	0.6	Traces	–
4	1	0.5	$(CH_3)_2CO$ 30	100	12	0.4	–	0.2
5	1	0.5	Dioxane 50	100	20	0.25	0.3	–
			trans-1,2-diphenylvinylmercury chloride					
6	1.5	0.95	C_2H_5OH 60	70	3	–	0.35	0.75
7	1	0.65	C_2H_5OH + HCl gas 30	100	5	0.35	Traces	–
8	1	0.65	$(CH_3)_2CO$ 30	100	5	0.4	–	–

*R = ($C_6H_5CH = CC_6H_5$).

4. Reaction of cis-Bis(1,2-Diphenylvinyl)mercury and of cis-1,2-Diphenylvinylmercury Chloride with Stannous Chloride. All of the experiments were carried out in sealed tubes. At the end of the heating period the tubes were opened, the precipitate of mercury was filtered off (in all of the experiments the yield of mercury was almost quantitative), and solvent was removed under reduced pressure (all treatments were carried out at room temperature). The residue was extracted with benzene, and the benzene was removed. Also, in Experiments 1 and 5 (Table 2) the residue, which did not contain tin, was isomerized into trans-stilbene by means of iodine in chloroform in sunlight. In Experiments 2, 4, and 6 the residue was treated with excess of aqueous ammonia, and the precipitate that formed was filtered off; cis-stilbene was extracted from the residue with ether and isomerized into trans-stilbene, and, with the aid of chloroform, the residue was separated into soluble α-stilbenestannonic acid and insoluble bis(1,2-diphenylvinyl)tin oxide. In Experiments 3 and 7, 1,2-diphenylvinyltin trichloride was isolated directly from the residue by repeated recrystallization from heptane. The results of the experiments are given in Table 2.

1,2-Diphenylvinyl tin trichloride melts at 108-110°, is very soluble in benzene, chloroform, and carbon tetrachloride, and is of good solubility in ethanol, methanol, and heptane.

Found %: C 41.60; 41.63; H 2.78; 2.72; Cl 25.69; 25.68
$C_{14}H_{11}SnCl_3$. Calculated %: C 41.56; H 2.72; Cl 26.34

α-Stilbenestannonic acid melts at 157-160° (not sharp). It is readily soluble in chloroform, carbon tetrachloride, ether, and benzene, and is insoluble in alcohol and petroleum ether.

Found %: Sn 35.55; 35.63
$C_{28}H_{22}SnO_2$. Calculated %: Sn 35.87

Bis(1-2-diphenylvinyl)tin oxide does not melt, even above 300°; it is insoluble in organic solvents.

Found %: Sn 23.91; 23.85

$C_{28}H_{22}SnO$. Calculated %: Sn 24.07

TABLE 2

Expt. No.	Amount of: Mercury compound (g)	$SnCl_2$ (g)	Solvent (ml)	Temperature (°C)	Time (hrs)	Yield of cis isomers(g): R*H	$RSnCl_3$	$RSnOOH$	R_2SnO
				cis-bis(1,2-diphenylvinyl)mercury					
1	2	1	C_2H_5OH 80	80	2.5	1	–	–	–
2	4	2	$(CH_3)_2CO$ 160	15-20	12	0.7	–	1.15	0.7
3	4	2	$(CH_3)_2CO$ 160	80	2	–	1.05	–	–
4	4	2	$(CH_3)_2CO$ 160	80	2	Little	–	2.2	–
				cis-1,2-diphenylvinylmercury Chloride					
5	2	1.3	C_2H_5OH 60	80	2.5	0.6	–	–	–
6	3.5	2.25	$(CH_3)_2CO$ 140	15-20	12	0.47	–	0.75	0.37
7	4	2.6	$(CH_3)_2CO$ 160	80	2	–	0.45	–	–

*R = $(C_6H_5CH = CC_6H_5)$.

5. Reaction of α-Stilbenestannonic Acid and of Bis(1,2-diphenylvinyl)tin Oxide with Thionyl Chloride. A solution of 4.5 g (0.036 mole) of $SOCl_2$ in 25 ml of petroleum ether was added to a suspension of 3 g (0.009 mole) of α-stilbenestannonic acid in 10 ml of petroleum ether. The mixture was heated for 90 minutes at 60-70°. The petroleum ether and excess of $SOCl_2$ were then removed under reduced pressure. The product was 3.2 g (88%) of 1,2-diphenylvinyltin trichloride, m.p. 109-110° after recrystallization from heptane.

Under the same conditions, 2 g (0.004 mole) of bis(1,2-diphenylvinyl)tin oxide and 0.74 g (0.006 mole) of $SOCl_2$ in 20 ml of petroleum ether yielded 1.17 g of 1,2-diphenylvinyltin trichloride, m.p. 107-109.5° after recrystallization from heptane (the melting point was not depressed by admixture of the substance obtained from α-stilbenestannonic acid).

6. Hydrolysis of 1,2-Diphenylvinyltin Trichloride. Excess of aqueous ammonia was added to a solution of 3 g of 1,2-diphenylvinyltin trichloride in 20 ml of alcohol. The precipitate that formed was filtered off, dried, and recrystallized from a mixture of benzene and alcohol. The product was 2.35 g (97%) of α-stilbenestannonic acid, m.p. 158-160° (not sharp). A mixture test showed no depression.

7. Reaction of 1,2-Diphenylvinyltin Trichloride with Mercuric Chloride. Hot solutions of 1.5 g (0.0037 mole) of 1,2-diphenylvinyltin trichloride in 25 ml of alcohol and 1 g (0.0037 mole) of mercuric chloride in 5 ml of alcohol were mixed, and the mixture was boiled for 1-2 minutes and then set aside at room temperature for 12 hours. Alcohol was removed under reduced pressure. The residue was treated with boiling benzene, and the benzene was evaporated. The product, amounting to 1.35 g (87%), was cis-1,2-diphenylvinylmercury chloride, m.p. 129-130° after recrystallization from alcohol (no depression in a mixture test).

8. Reaction of α-Stilbenestannonic Acid and of Bis(1,2-Diphenylvinyl)tin Oxide with Mercuric Oxide. Boiling aqueous 5 N NaOH (100 ml) was added to a suspension of 2 g (0.0006 mole) of α-stilbenestannonic acid in

32 ml of alcohol, and to the resulting mixture a hot solution of 0.82 g (0.003 mole) of $HgCl_2$ in 24 ml of alcohol was added. The mixture was boiled for 1-2 minutes, and was then diluted with water. The precipitate was filtered off and dried. It was treated several times with boiling benzene, benzene was evaporated off, and the residue was recrystallized from a mixture of benzene and alcohol. The product, amounting to 1.5 g (89%) was cis-bis(1,2-diphenylvinyl)mercury, m.p. 145-146° (undepressed in a mixture test).

Under the same conditions, 1 g (0.002 mole) of bis(1,2-diphenylvinyl)tin oxide in 16 ml of ethanol, 50 ml of 5 N NaOH, and 0.55 g (0.002 mole) of $HgCl_2$ in 16 ml of alcohol yielded 0.76 g (67%) of cis-bis(1,2-diphenylvinyl)mercury.

9. Reaction of the Stereoisomeric Bis(1,2-diphenylvinyl)mercurys with Mercuric Bromide. A mixture of 3 g (0.0053 mole) of trans-bis(1,2-diphenylvinyl)mercury, 2.1 g (0.0058 mole) of $HgBr_2$, and 51 ml of absolute alcohol was heated in a sealed tube in a boiling water bath for 5.5 hours. The crystals that formed were filtered off, the filtrate was evaporated down, and the residue was treated with benzene. The substance remaining after evaporation of the benzene was added to the main bulk of the crystals, and the whole mass was crystallized twice from alcohol. The product, amounting to 4.8 g (98%) was 1,2-diphenylvinylmercury bromide, m.p. 157-158°. This substance is soluble in alcohol, benzene, and chloroform.

	Found %:	C 36.72; 36.89; H 2.43; 2.52
$C_{14}H_{11}HgBr$.	Calculated %:	C 36.58; H 2.39

Under the same conditions, 2 g (0.0035 mole) of cis-bis(1,2-diphenylvinyl)mercury and 1.35 g (0.0038 mole) of $HgBr_2$ in 34 ml of absolute alcohol yielded 4.85 g (95%) of 1,2-diphenylvinylmercury bromide, m.p. 118-120° after two crystallizations from alcohol. This substance is soluble in alcohol, benzene, and chloroform.

	Found %:	C 36.62; 36.74; H 2.52; 2.53
$C_{14}H_{11}HgBr$.	Calculated %:	C 36.58; H 2.39

10. Symmetrization of the Stereoisomeric 1,2-Diphenylvinylmercury Halides. a) Symmetrization of the Stereoisomeric 1,2-Diphenylvinylmercury Bromides with Potassium Iodide. A solution of 3.35 g (0.02 mole) of potassium iodide in 54 ml of acetone and 6.5 ml of water was added to a solution of 2 g (0.0021 mole) of the 1,2-diphenylvinylmercury bromide of m.p. 157-158° in 150 ml of acetone and 10 ml of water. The mixture stood at room temperature for one day. The precipitate was then filtered off and dried. The product, amounting to 1.2 g (93%), was trans-bis(1,2-diphenylvinyl)mercury, m.p. 239-241° after recrystallization from dioxane.

An experiment on the low-melting 1,2-diphenylvinylmercury bromide was carried out with the same amounts, but, owing to the appreciable solubility of cis-bis(1,2-diphenylvinyl) mercury in aqueous acetone, at the end of the reaction the reaction mixture was diluted with water and the precipitate filtered off. The substances obtained were cis-bis(1,2-diphenylvinyl)mercury, amounting to 0.65 g (53%) (m.p. 145-146° after recrystallization from a mixture of benzene and alcohol), and unchanged 1,2-diphenylvinylmercury bromide (m.p. 119-120°; 0.95 g, i.e. 7.5% of the amount taken).

b) Symmetrization with Sodium Stannite. A solution of Na_2SnO_2 (prepared from 3 g of $SnCl_2 \cdot 2H_2O$ and 7.5 g of NaOH in 75 ml of water) was added to a solution of 2.2 g of cis-1,2-diphenylvinylmercury chloride in 40 ml of alcohol. The mixture was set aside for 36 hours. The precipitate was then filtered off, dried, and carefully extracted with boiling benzene. The benzene was evaporated, and the residue, recrystallized from a mixture of benzene and alcohol, gave 1.2 g (95%) of cis-bis(1,2-diphenylvinyl)mercury, m.p. 145-147°.

Under the same conditions, the 1,2-diphenylvinylmercury bromide of m.p. 118-120° gave cis-bis(1,2-diphenylvinyl)mercury in 94% yield.

Trans-1,2-diphenylvinylmercury chloride and the 1,2-diphenylvinylmercury bromide of m.p. 157-158° were symmetrized with sodium stannite to the extent of 65-70%, the product being trans-bis(1,2-diphenylvinyl)-mercury.

c) Symmetrization with Ammonia. Ammonia gas was passed for two hours through a solution of 2 g of trans-1,2-diphenylvinylmercury chloride in 80 ml of chloroform. The solution was diluted with water, and the precipitate was filtered off, dried, and carefully extracted with boiling xylene. Xylene was removed under reduced pressure, and the residue was recrystallized from dioxane. The product, amounting to 0.8 g (59%), was trans-bis(1,2-diphenylvinyl)mercury, m.p. 240-241°. Under the same conditions, 1,2-diphenylvinylmercury

TABLE 3

Expt. No.	Amount of: Organometallic cpd. mole	Solvent (ml)	$C_6H_4O_2Br_2$ (mole)	dioxane (ml)	Time (hrs)	Temperature (°C)	Yield (g): HgS	R*HgBr	RBr
			trans-bis(1,2-diphenylvinyl)mercury						
1	0.0036	70	0.0072	30	48	15-20	0.27	trans-1.05	trans-1.10
2	0.0036	70	0.0144	30	0.25	101	0.82	–	trans-1.8
3	0.0036	70	0.0072	25	1	80	0.82	–	trans-1.65
4	0.0036	70	0.0036	15	12	15-20	Traces	trans-1.55	not isolated
			trans-1,2-diphenylvinylmercury chloride						
5	0.0036	50	0.0044	15	1	80	0.83	–	trans-0.75
			trans-1,2-diphenylvinylmercury bromide						
6	0.0021	35	0.0022	15	1	80	0.48	–	trans
			cis-bis(1,2-diphenylvinyl)mercury						
7	0.0036	70	0.0072	25	3	15-20	0.83	–	cis-1.67
8	0.0072	140	0.0144	50	1.5	15-20	1.67	–	cis-3.45
9	0.0036	70	0.0036	15	1.5	15-20	Traces	cis-1.55	cis
			cis-1,2-diphenylvinylmercury chloride						
10	0.0043	60	0.0044	25	2	15-20	1	–	cis-0.95
			cis-1,2-diphenylvinylmercury bromide						
11	0.0021	35	0.0022	15	1.5	15-20	0.5	–	cis
			cis-1,2-diphenylvinyltin trichloride						
12	0.0099	20	0.0098	40	1	70	–	–	cis-2.25
			cis-α-stilbenestannonic acid						
13	0.009	20	0.009	35	1	70	–	–	cis-2.08
			cis-bis(1,2-diphenylvinyl)tin oxide						
14	0.003	17	0.008	25	1	70	–	–	cis-1.25

*R = ($C_6H_5CH = CC_6H_5$).

bromide of m.p. 157-158° gave trans-bis(1,2-diphenylvinyl)mercury in 60% yield. Cis-1,2-diphenylvinylmercury chloride and low-melting 1,2-diphenylvinylmercury bromide gave cis-bis(1,2-diphenylvinyl)mercury in 88% yield.

11. Reaction of Dioxane Dibromide with Organotin and Organomercury Derivatives of the Stereoisomeric Stilbenes. All of the experiments with dioxane dibromide were carried out in the same way. To a solution (or suspension) of the organometallic compound in dioxane (mercury compounds) or benzene (tin compounds), a dioxane solution of dioxane dibromide was added. When reaction was complete, solvent was removed under reduced pressure and the residue was treated with 3% HCl and ether. From the aqueous layer the metal sulfide was precipitated with H_2S (HgS was precipitated quantitatively, dried, and weighed). The stereoisomeric α-bromostilbenes - and in some experiments the stereoisomeric 1,2-diphenylvinylmercury bromides - were isolated from the ether layer. The α-bromostilbenes were extracted from the mixture with petroleum ether and were recrystallized from methanol cooled with solid carbon dioxide. The 1,2-diphenylvinylmercury bromides were recrystallized from alcohol. The results of the experiments are given in Table 3.

12. Reaction of trans-Bis(1,2-diphenylvinyl)mercury with Bromine. To a suspension of 2 g (0.0036 mole)

of trans-bis(1,2-diphenylvinyl)mercury in 70 ml of benzene, 1.15 g (0.0072 mole) of bromine was added at room temperature. The solution was decolorized immediately, and the precipitate disappeared. The mixture was set aside for 90 minutes, after which time it was treated with 3% HCl; the layers were separated. Hydrogen sulfide precipitated 0.82 g (38%) of HgS. From the benzene layer, 1.7 g (91%) of trans-α-bromostilbene, m.p. 30-32°, was isolated.

SUMMARY

1. By the reaction of cis-bis(1,2-diphenylvinyl)mercury and of cis-1,2-diphenylvinylmercury chloride with stannous chloride, cis-1,2-diphenylvinyltin trichloride, cis-α-stilbenestannonic acid, and cis-bis(1,2-diphenylvinyl)tin oxide were prepared.

2. By reaction of the stereoisomeric bis(1,2-diphenylvinyl)mercurys with mercuric bromide, the stereoisomeric 1,2-diphenylvinylmercury bromides were prepared.

3. It was shown that mercury derivatives of the stereoisomeric stilbenes do not give organothallium and organotin derivatives when treated with $TlCl_3$ and tin-sodium alloy, respectively. Trans-bis(1,2-diphenylvinyl)-mercury and trans-1,2-diphenylvinylmercury chloride do not give organotin compounds when treated with stannous chloride.

4. The reaction of mercury and tin derivatives of the stereoisomeric stilbenes with dioxane dibromide was investigated, and it was shown that it results in the formation of the stereoisomeric α-bromostilbenes.

5. The behavior of the metal derivatives of stilbene that we have studied is in accord with the rule relating to the preservation of geometric configuration in electrophilic and radical exchange reactions.

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2-AMINOVINYL KETONES

COMMUNICATION 4. SYNTHESIS OF KETONES OF THE PYRIDINE SERIES

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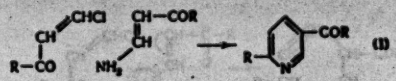
and A.N. Nesmeyanov

2-Aminovinyl ketones are now readily accessible owing to the recent development in our laboratory of a method for their synthesis [1]. In the present paper we describe a new synthesis of ketones of the pyridine series based on the reaction between 2-aminovinyl ketones and 2-chlorovinyl ketones, which have been studied in our laboratory during recent years. These compounds react together without the aid of any condensing agent even at room temperature. In the case of 2-chlorovinyl methyl ketone and 2-aminovinyl methyl ketone, a substance corresponding in properties to 5-acetyl-2-methylpyridine can be isolated from the reaction mixture. The picrate and oxime of this substance were found to have the same constants as those cited in the literature. The yield of 5-acetyl-2-methylpyridine attained 50%. The reaction was found to be fairly general.

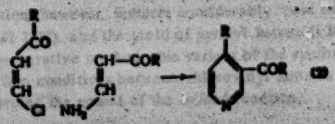


(1)

R = CH_3, C_2H_5, C_3H_7, C_5H_{11}

The best results were obtained under the following conditions. A mixture of the alkyl 2-chlorovinyl ketone and double the amount of the alkyl 2-aminovinyl ketone, without addition of solvent, was allowed to stand at room temperature. After a few hours precipitation began of the amine hydrochloride formed from the liberated hydrogen chloride, which was taken up by the excess of the 2-aminovinyl ketone. After several days precipitation ceased and, if considered necessary, the mixture was heated for a few hours in a water bath in order to complete the reaction. The reaction mixture was heated with dilute sulfuric acid in order to separate the pyridine derivative from other reaction products, and the pyridyl ketone was isolated from the acid solution by the usual method and was purified by distillation. By this method, starting from ethyl, propyl, and pentyl 2-aminovinyl ketones and the corresponding alkyl 2-chlorovinyl ketones, we prepared the corresponding 5-acyl-2-alkylpyridines in satisfactory yields.

As it is possible that the reaction between a 2-aminovinyl ketone and a 2-chlorovinyl ketone may proceed in a different direction with formation of a 3-acyl-4-alkylpyridine in accordance with the equation



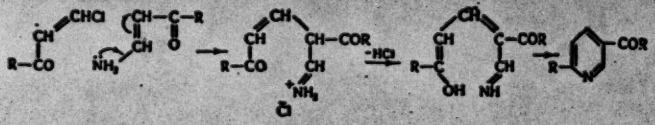
(2)

The structure of the compounds obtained was in need of confirmation. We therefore submitted one of these compounds – ethylpropionylpyridine – to permanganate oxidation, which should yield either isocinchomeronic or cinchomeronic acid, depending on which of the two possible structures is correct. The acid obtained, which was

isolated from the oxidation products in 54% yield, corresponded in properties to isocinchomeronic acid, and, in final confirmation of its identity, its dimethyl ester was prepared and found to be a solid melting at 162° (dimethyl cinchomeronate is a liquid). It was thus established that the compounds that we had prepared were 5--acyl-2-alkylpyridines and that the reaction proceeds in accordance with the first scheme.

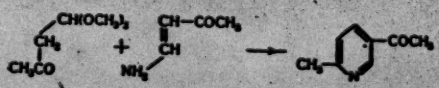
The reaction investigated is of interest from the preparative point of view, for reported methods for the synthesis of ketones of the pyridine series, particularly alkylpyridyl ketones, have not been adequately developed [2]. Our reaction is similar in character to that described by Benary for the synthesis of ketones of the pyridine series by the action of ammonia on hydroxymethylene ketones [3-5]. Benary's reaction has not been developed sufficiently to be regarded as a satisfactory method of synthesis, for the author gives no precise details of the yields of products and in some cases does not give their constants; moreover, it is known that by-products are formed in this reaction. The method that we have proposed has also the indisputable advantage that the original 2-chlorovinyl and 2-aminovinyl ketones are readily accessible; furthermore, their structures do not need special proof, whereas it is generally necessary to prove the structure of the hydroxymethylene ketone in each separate case and such structures have been the subject of dispute until quite recently (see, for example [6]).

The fact that 2,5- and not 3,4-substituted pyridines are formed in our reaction enables us to make some suggestions regarding the course of the reaction. It should be noted the reaction is similar to the condensation carried out earlier in our laboratory between 2-chlorovinyl ketones and 3-aminocrotonic ester, which yielded 2,6-dialkylnicotinic acids [7]. Since 2-aminovinyl ketones, being α,β-unsaturated β-amino compounds, are similar in character and behavior to 3-aminocrotonic ester, it is quite to be expected that the result will be the same in both the cases that we have studied: the alkyl radical and oxygen function will be in the 2,5-positions of the pyridine nucleus formed. It is well known that both derivatives of 3-aminocrotonic ester [8] and derivatives of 2-aminovinyl ketones [9] are alkylated with transfer of the reaction center to the α-carbon atom. It may be considered that, in our case also, the 2-aminovinyl ketone is first "ketovinylated" at the α-carbon atom, and the resulting derivative of an unsaturated δ-diketone undergoes redistribution of bonds and ring closure with formation of the energetically more favorable aromatic pyridine system. This view is expressed in the scheme:



An analogous scheme can be given for the condensation of 2-chlorovinyl ketones with 3-aminocrotonic ester, referred to above [7].

We have studied one example of the condensation of 2-aminovinyl ketones with β-keto acetals, which are readily accessible, being prepared from 2-chlorovinyl ketones [10]. It was found that the condensation of 2-aminovinyl methyl ketone with acetoacetaldehyde dimethyl acetal again yielded 5-acetyl-2-methylpyridine, identical with the substance prepared by the method described above.



This reaction, however, requires considerably more severe conditions (heating a mixture of the reactants for many hours at 135°), and the yield of pyridyl ketone is lower. As this reaction is inferior to the one already described as a preparative method, this variant of the synthesis was not developed further. The great difference in the condensation conditions between chlorovinyl ketones and β-keto acetals makes it impossible to make any suggestions regarding the course of the second reaction.

EXPERIMENTAL

5-Acetyl-2-methylpyridine. A mixture of 14.3 g (0.137 mole) of 2-chlorovinyl methyl ketone and 23.3 g (0.274 mole; 100% excess) of 2-aminovinyl methyl ketone was allowed to stand for two days at room tempera-

ture. The thick dark-colored reaction mixture was then boiled for 5 minutes with excess of 20% sulfuric acid, cooled, and extracted three times with ether. The aqueous layer was made alkaline with 40% aqueous caustic soda and extracted with ether; the extract was dried over potassium carbonate. The ether was distilled off, and the residue was vacuum-distilled, a fraction boiling at 95-97° (5 mm) being collected. The yield was 9.4 g (50.8%). After redistillation the 5-acetyl-2-methylpyridine had the following constants: b.p. 95-96° (5 mm); n_D^{20} 1.5319; d_4^{20} 1.0681.

Found %: C 70.76; 70.91; H 6.82; 6.76
C_8H_9ON. Calculated %: C 71.08; H 6.73

For 5-acetyl-2-methylpyridine the literature [3] gives b.p. 231-232°.

The oxime was prepared by heating the substance for two hours with hydroxylamine in aqueous alcohol; colorless needles, m.p. 183° (from 40% alcohol).

Found %: N 18.58; 18.85
$C_8H_{10}ON_2$. Calculated %: N 18.66

The literature [3] gives m.p. 182°.

The picrate was prepared in alcoholic solution; yellow crystals, m.p. 190° (from alcohol).

The literature [3] gives m.p. 190°.

2-Ethyl-5-propionylpyridine. This was prepared similarly from 9.3 g (0.078 mole) of 2-chlorovinyl ethyl ketone and 15.4 g (0.156 mole) of 2-aminovinyl ethyl ketone. Reaction was allowed to proceed for three days. The mixture was treated as indicated above. In the vacuum distillation the fraction boiling at 115-115° (8 mm) was collected, the yield being 10.2 g (80%). After redistillation the 2-ethyl-5-propionylpyridine had the following constants: b.p. 113-115° (7 mm); n_D^{20} 1.5160; d_4^{20} 1.0200.

Found %: C 73.07; 72.86; H 7.98; 8.09
$C_{10}H_{13}ON$. Calculated %: C 73.00; H 7.98

For 2-ethyl-5-propionylpyridine the literature [4] gives b.p. 247-248°.

The oxime was prepared as before; colorless needles, m.p. 102.5° (from 40% alcohol).

Found %: N 16.00; 15.83
$C_{10}H_{14}ON_2$. Calculated %: N 15.73

The literature [4] gives m.p. 104°.

5-Butyryl-2-propylpyridine. This was prepared similarly from 26.4 g (0.20 mole) of 2-chlorovinyl propyl ketone and 46 g (0.40 mole) of 2-aminovinyl propyl ketone. Reaction was allowed to proceed for seven days. The mixture was treated as before, and in the vacuum distillation the fraction boiling at 133-134° (8 mm) was collected, the yield being 15.5 g (41%). After redistillation the 5-butyryl-2-propylpyridine had the following constants: b.p. 134-135° (8 mm); n_D^{20} 1.5117; d_4^{20} 0.9877.

Found %: C 75.21; 75.07; H 8.72; 8.80
$C_{12}H_{17}ON$. Calculated %: C 75.35; H 8.96

For 5-butyryl-2-propylpyridine the literature [5] gives b.p. 152° (13 mm); d_4^{20} 0.9782.

The oxime was prepared as before; colorless needles, m.p. 88.5° (from 40% alcohol).

Found %: N 13.79; 13.95
$C_{12}H_{18}ON_2$. Calculated %: N 13.60

The literature [5] gives m.p. 84-86°.

5-Hexanoyl-2-pentylpyridine. This was prepared similarly from 6.8 g (0.042 mole) of 2-chlorovinyl pentyl ketone and 11.9 g (0.085 mole) of 2-aminovinyl pentyl ketone. Reaction was allowed to proceed for seven days. The mixture was boiled with 90 ml of dilute hydrochloric acid (1:5). Further treatment was as before, and in the vacuum distillation the fraction boiling at 183-184° (6 mm) was collected, the yield being 1.9 g (18.3%) (when reaction was allowed to proceed for only three days, the yield was 14%). After redistillation the 5-hexanoyl-2-pen-

tylpyridine had the following constants: b.p. 158-159° (3 mm); n_D^{20} 1.5010; d_4^{20} 0.9464.

Found %: C 77.54; 77.42; H 10.39; 10.32
$C_{10}H_{13}ON$. Calculated %: C 77.73; H 10.16

Reaction of 2-Chlorovinyl Methyl Ketone with Acetoacetaldehyde Dimethyl Acetal. A mixture of 25.5 g (0.20 mole) of acetoacetaldehyde dimethyl acetal and 24.7 g (0.29 mole) of 2-chlorovinyl methyl ketone was heated at 135° for 70 hours. When cool, the reaction mixture was extracted with ether, and the ether extract was dried over potassium carbonate. The ether was distilled off, and the residue was vacuum-distilled, the fraction boiling at 103-106° (7 mm) being collected. The yield was 8.6 g (31.5%). After redistillation the 5-acetyl-2-methylpyridine had the following constants: b.p. 85-85.5° (3 mm); n_D^{20} 1.5320; d_4^{20} 1.0664.

The oxime was prepared in the usual way: m.p. 182°, undepressed by admixture with the oxime of 5-acetyl-2-methylpyridine prepared from 2-aminovinyl methyl ketone.

The picrate was prepared in the usual way: m.p. 190°, undepressed by admixture with the picrate of 5-acetyl-2-methylpyridine prepared from 2-aminovinyl methyl ketone.

Oxidation of 2-Ethyl-5-propionylpyridine. Potassium permanganate (51.4 g) was added to a mixture of 6.13 g of 2-ethyl-5-propionylpyridine and 600 ml of water. The mixture was heated at 70° for two hours and was then boiled until decolorized. Manganese dioxide was filtered off and treated with boiling water. The combined filtrates were evaporated down to 200 ml. Concentrated hydrochloric acid (50 ml) was added to the hot solution, and the mixture was allowed to stand in a refrigerator for three days. The precipitate of acid was filtered off and dried at 90° (10 mm). The yield was 3.3 g (54%); m.p. 243°.

As the melting point data in the literature are very inconsistent and as there are indications [11] that the pure acid cannot be prepared by recrystallization, we converted our sample into the dimethyl ester. A mixture of 2.5 g of the acid, 48.6 ml of absolute methanol, and 2 ml of concentrated sulfuric acid was boiled for three hours. When the mixture was cooled, a precipitate formed and was filtered off and washed with methanol. Recrystallization from absolute methanol gave colorless needles, m.p. 162°. For dimethyl isocinchomeronate the literature [11] gives m.p. 164°.

SUMMARY

1. The reaction of alkyl 2-aminovinyl ketones with alkyl 2-chlorovinyl ketones was investigated. It provides a method for the synthesis of 5-acyl-2-alkylpyridines.

2. The structure of the products was confirmed by the oxidation of one of them to isocinchomeronic acid.

3. It was shown that the condensation of 2-aminovinyl methyl ketone with acetoacetaldehyde dimethyl acetal yields 5-acetyl-2-methylpyridine.

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SEPARATION OF AMINO CARBOXYLIC ACIDS FROM AMMONIUM CHLORIDE WITH THE AID OF CATION - EXCHANGE RESINS

E.I. Vasilyeva and R.Kh. Freidlina

In the ammonolysis of chloro carboxylic acids, the corresponding amino acids are formed in admixture with ammonium chloride. As is well known, when the amino carboxylic acid and ammonium chloride have very similar solubilities in the solvents generally used for their separation (methanol, diethylamine, etc.), the separation is effected by treatment of the mixture with excess of lead oxide or silver oxide. This method is very laborious and is not always successful.

In recent years, increasing application has been found for ion-exchange resins for the isolation and separation of mixtures of amino carboxylic acids [1]. There is very little information in the literature regarding the isolation of amino carboxylic acids from their hydrochlorides and the separation of amino carboxylic acids from ammonium chloride with the aid of ion-exchange resins. We may here mention papers describing the use of anionites for the isolation of alanine [2] and ε-aminohexanoic acid [3] from their pure hydrochlorides or from the hydrochloride in admixture with ammonium chloride [2].

As far as we know, the separation of amino carboxylic acids from ammonium chloride with the aid of cation-exchange resins has not been described. The use of sulfocationites for this purpose appeared to us to be particularly attractive in view of the ready availability of various cation-exchange resins of this type having high capacity, mechanical strength, chemical stability, and other necessary qualities. It is known that sulfocationites can bind amino acids fairly firmly, so that it should be possible to separate amino acids from admixed acid and neutral substances simply by elution of the column with water after the solution containing the amino acid has been passed through.

By the use of the cationites SBS and SDV-3*, which contain sulfo groups, we succeeded in separating glycine, norvaline, 7-aminoheptanoic acid, and 9-aminononanoic acid from admixed ammonium chloride. We isolated these amino acids both from equimolecular mixtures of amino acid and ammonium chloride, and also from the reaction mixtures obtained by the ammonolysis of the corresponding chloro carboxylic acids with aqueous ammonia. In the second case the content of amino acid in the reaction mixture was determined in an aliquot by the van Slyke method. It was shown also that it is possible to isolate free 7-aminoheptanoic acid from its hydrochloride with the aid of the same cationites.

EXPERIMENTAL

Most of the experiments were carried out in columns containing 35-40 g of air-dry resin. The height of the column in a tube of diameter 2 cm was 35-40 cm. The loading and operation of the column were carried out in the usual way [4]. We studied the capacity of the cationite SBS both with respect to 7-aminoheptanoic acid, and also with respect to ammonium chloride. The dynamic capacity with respect to ammonium chloride was determined by titration of hydrochloric acid in the effluent.

It was found to be convenient to follow the course of the absorption and desorption of 7-aminoheptanoic acid by its qualitative reaction with ninhydrin, which is applicable to ω-amino as well as α-amino carboxylic acids. The amount of amino acid bound by the cationite was determined by washing the cationite with 5% am-

*All of the resins that we have examined were kindly provided by I.P. Losev, E.B. Trostyanskaya, and A.S. Tevlina, to whom we express our sincere thanks.

monia to bring about the desorption of the amino acid and then evaporating the eluate. The capacity with respect to 7-aminoheptanoic acid was found to be 125 mg per gram of resin for the passage of a 6% solution at 2 ml/min.sq.cm. The capacity with respect to ammonium chloride was found to be 50 mg per gram of resin for the passage of a 3% solution at 2-7 ml/min.sq.cm.

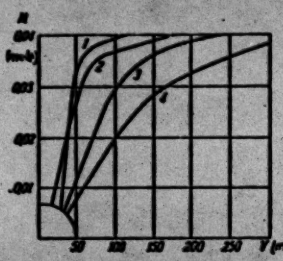

Fig. 1. Yield curves for: 1) glycine; 2) 7-aminoheptanoic acid; 3) norvaline; 4) 9-aminononanoic acid.

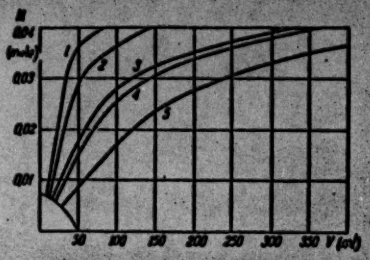

Fig. 2. Yield curves for 7-aminoheptanoic acid on the cationites: 1) SDV-1; 2) MSF; 3) SBSR; 4) SBS; 5) RF.

Using mixtures of 7-aminoheptanoic acid and ammonium chloride, we studied the effect of concentration and rate of passage on the dynamic capacity of the resin with respect to amino acid, and also the effect of the rate of passage and of the concentration of ammonia on the completeness of the removal of amino acid. The mixture to be separated contained 70% of 7-aminoheptanoic acid and 30% of ammonium chloride(Table 1).

These experiments showed that increase in the ammonia concentration from 5% to 10% did not reduce the volume of solution required for elution (Experiments 1 and 3) and that it was best to elute at a linear rate of passage of 1-1.5 ml/min.sq.cm. (Experiments 2, 5, and 6), but increase in the rate of passage to greater than 1.5-2 ml/min.sq.cm causes the amount of the amino acid passing into the effluent to increase (Experiments 2, 3, and 4).

Fig. 1 shows the yield curves for glycine, norvaline, 7-aminoheptanoic acid, and 9-aminononanoic acid on the cationite SDV-3. It will be seen that the acid that is most readily desorbed by ammonia is glycine (Curve 1), and the most difficultly desorbed acid is 9-aminononanoic acid (Curve 4). It will be seen also that in the first half of the whole volume of the eluate there is 75-90% of the total amount of amino acid to be eluted.

Fig. 2 presents the yield curves for 7-aminoheptanoic acid on the cationites SBS, SBSR, SDV-1, MSF, and RF. Some data characterizing these cationites have been reported in the literature [5-8]. It will be seen from Fig. 2 that the amino acid is most readily desorbed from SDV-1, and is most difficultly desorbed from RF.

Capacities with respect to 7-aminoheptanoic acid were determined for these cationites, and the results are shown in Table 2. The best results were obtained for the cationite SDV-1.

Some experiments on the purification of amino acids from ammonium chloride were carried out on a larger scale, and these showed that the results obtained in large columns were in accord with those obtained in 40-g columns. It was found that in the large columns the amount of 5% ammonia required for the complete desorption of the amino acids was very much less, since the dilute eluates could be used again in the following elution cycle. The results obtained are compared in Table 3, which shows that the proposed method for the separation of amino acids from ammonium chloride is applicable both to α-amino acids (Experiments 1 and 2) and to ω-amino acids (Experiments 3-5). In all cases the amino acids were recovered in 95-99% yield and they did not contain chlorine (Experiments 1-5). The isolation of amino acids from the reaction mixture obtained in the ammonolysis of the corresponding chloro carboxylic acids was also very satisfactory (Experiments 3-5).

From Table 3 it will be seen also that cationites containing sulfo groups are able to absorb amino acids from their hydrochlorides (Experiment 6). Thus, by passing pure 7-aminoheptanoic acid hydrochloride through the cationite SBS, 7-aminoheptanoic acid was obtained in 96% yield, and the resulting preparation was completely free from chloride ions.

TABLE 1

Expt. No.	Amount of mixture (g)	Concentration of mixture (%)	Linear rate of passage (ml/min. sq.cm)	Amount leaving column (g)	Concentration of aqueous NH_3 (%)	Linear rate of passage (ml/ min. sq.cm)*	Volume of eluate (ml)	Amount of amino acid obtained (g)**	Capacity with respect to amino acid (mg/g resin)
1	4.8	10	1.5-2	—	10	1-1.5	350	2.86	71
2	6	10	1.5	0.40	10	4	425	3.37	84
3	6	10	3	0.77	5	1-1.5	335	3.13	78
4	6	10	8	1.62	5	1-1.5	325	2.60	82
5	6	15	1.5-2	0.37	5	1-1.5	375	3.80	95
6	2	5	1.5-2	0.10	5	1.5	220	1.26	97

*Experiments 1-5 were carried out in a column containing 40 g of resin. In Experiment 6 the column contained 13 g of resin.
**The acid obtained melted at 183-184°, and the original acid at 186-187°.

TABLE 2

Cationite	Amount of resin (g)	Amount of mixture* (g)	Concentration of mixture (%)	Amount leaving column (g)	Volume of eluate** (ml)	Amount of amino acid obtained (g)	Capacity with respect to amino acid (mg/g resin)
MSF	40	8	10	0.04	150	5.53	138
SDV-1	38	8	10	—	100	5.55	158
SBSR	35	5.8	10	1.0	200	3.24	92
SBS	30	4.5	10	—	200	3.11	103
RF	6	2.5	10	0.65	140	1.0	62

*The mixture contained 70% of amino acid and 30% of ammonium chloride. The solution of the mixture was passed through the cationite at a rate of 1.5-2 ml/min.sq.cm.
**Elution was carried out at a rate of 1-1.5 ml/min.sq.cm.

TABLE 3*

Expt. No.	Cationite	Amount of mixture (g)	Amount of amino acid in mixture (g)	Amino Acid	Overall concentration of solution (%)	Rate of elution (ml/min)	Volume of eluate (ml)	Amt. of amino acid (g)	Amt. of amino acid (%)
1	SDV-3	5	3	Glycine	10	5-6	150	2.97	99
2	SDV-3	7	4.9	2-Aminovaleric acid	10	5-6	200	4.85	99
3**	SBS	—	5	7-Aminoheptanoic acid	10	4-5	220	4.90	98
4**	SDV-3	—	5.5	7-Aminoheptanoic acid	10	4-5	100	5.45	99
5**	SDV-3	—	16.3	9-Aminononanoic acid	6	15	700	15.52	95
6***	SBS	—	4	7-Aminoheptanoic acid	7	4-5	200	3.87	96.7

*The table gives the mean results of several duplicate experiments.
**In these experiments the amino acids were obtained by ammonolysis of the corresponding chloro carboxylic acids. The content of ω-amino acid in the solution was determined by the Van Slyke method.
***Isolation of the amino acid from the pure hydrochloride.

SUMMARY

1. A method is proposed for the separation of a mixture of an amino acid and ammonium chloride with the aid of cation-exchange resins.

2. It is shown that some amino carboxylic acids can be isolated from their hydrochlorides with the aid of cation-exchange resins.

3. It is shown that the Soviet cationites SBS, SBSR, and SDV can be successfully applied for the separation of amino carboxylic acids from ammonium chloride.

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ADDITION OF MERCURY SALTS TO VINYL ETHERS

PREPARATION OF MERCURATED ACYLALS*

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The addition reaction of mercury salts in aqueous solution with substances containing an ethylene bond has been extensively investigated; the reaction results in the addition of a hydroxyl group and a residue of the mercury salt at the position originally occupied by the double bond. In this way olefins yield alcohols containing the residue of the mercury salt in the β-position [1]. When the medium is an alcohol [2] or amine [3] instead of water, the addition product contains an OR or NR_2 group instead of OH. The addition of mercury salts to olefins can be carried out also in a medium of aliphatic carboxylic acid [4]. In this case the double bond takes up a residue of the mercury salt and the acyloxy group corresponding to the acid used as medium.

A common feature of all of these reactions is the active participation of the solvent. The product always contains a residue of the solvent molecule (– OH, – OR, – NR_2, RCOO–) in its molecule. As regards the mechanism of the addition of mercury salts to ethylene bonds, on the basis of kinetic investigations it is generally considered that addition is preceded by reaction between the mercury salt and the solvent [5,6]. For reaction in an aqueous medium, therefore, the whole process can be represented as follows:

$$HgX_2 + H_2O \rightleftharpoons Hg\begin{matrix}X\\OH\end{matrix} + HX;$$

$$Hg\begin{matrix}X\\OH\end{matrix} + RCH = CH_2 \rightleftharpoons RCH(OH)CH_2HgX.$$

In a study of the addition of mercuric acetate to cyclohexene and styrene in dioxane, Wright [6] attempted to break down the addition reactions into its stages with the object of isolating intermediate products of the type $RCHXCH_2HgX$ and studying their hydrolysis (or alcoholysis), but no definite results were obtained. This type of direct addition of mercury salts without participation of the solvent is well known for compounds containing triple bonds and has been studied for hydrocarbons [7,8], alcohols [9], and ketones [10] of the acetylene series.

In view of the high reactivity of vinylethers, we considered that it would be possible to effect the addition of mercury salts to these compounds without the participation of the solvent, and so synthesize compounds of the type $XHgCH_2CH(OR)X$. Our experiments showed that mercuric acetate does indeed add rapidly at the double bond of a vinyl ether (methyl, ethyl, isopropyl, butyl, or phenylvinyl ether) as follows:

$$CH_2 = CHOR + (CH_3COO)_2Hg \rightarrow CH_2COOHgCH_2\begin{matrix}OR\\OCOCH_3\end{matrix}$$

By this reaction we have synthesized organomercury compounds of a new type - mercurated acylals - in almost quantitative yields. The reactions of methyl and ethyl vinyl ethers with mercuric acetate were carried out in

*Communication from Academician A.N. Nesmeyanov's Laboratory.

an absolute ether medium, the reaction with phenyl vinyl ether in absolute acetone, while the reactions of isopropyl and butyl vinyl ethers were carried out in absence of solvent. The mercurated acylals obtained from methyl, ethyl, and phenyl vinyl ethers are crystalline solids, and those obtained from the other two vinyl ethers are viscous oils. All of the compounds are rather unstable; they are readily hydrolyzed in the air, and they decompose within a few days when kept in a desiccator. When dissolved in water they are rapidly hydrolyzed to mercurated acetaldehyde.

The behavior of mercurated acylals towards certain reagents is interesting (for example, towards sodium iodide, triethyl phosphite, acetyl chloride, and caustic alkali). Under the action of these compounds mercurated acylals readily break down into the original reactants - the mercury salt and the vinyl ether. When mercurated acylals are treated with sodium iodide, the following reaction occurs:

$$CH_3COOHgCH_2CH(OR)OCOCH_3 + 4NaI \rightarrow CH_2 = CHOR + Na_2[HgI_4] + 2CH_3COONa.$$

The original vinyl ether is formed also when a mercurated acylal is treated with triethyl phosphite, and in addition, mercury and ethyl acetate are formed. The reaction can be represented as follows:

$$CH_3COOHgCH_2CH(OR)OCOCH_3 + P(OC_2H_5)_3 \rightarrow$$

$$\rightarrow CH_2 = CHOR + Hg + \left[\begin{matrix} CH_3COO & & OC_2H_5 \\ & P & \\ CH_3COO & & OC_2H_5 \end{matrix}\right] \downarrow$$

$$2CH_3COOC_2H_5 + (C_2H_5OPO_2)_x$$

Thus, we have a case here of alkylation by means of triethyl phosphite. A reaction carried out separately between mercuric acetate and triethyl phosphite also yielded ethyl acetate.

Under the action of acetyl chloride, mercurated acylals readily decompose as follows:

$$CH_3COOHgCH_2CH(OR)OCOCH_3 + CH_3COCl \rightarrow (CH_3CO)_2O + CH_2 = CHOR + CH_3COOHgCl.$$

The mercury salt that forms brings about the polymerization of the vinyl ether. If two molecular proportions of acetyl chloride are brought into reaction in one portion, instantaneous resinification of the liberated vinyl ether occurs.

When any of the mercurated acylals apart from that obtained from phenyl vinyl ether is treated with caustic alkali, mercuric oxide is precipitated.

Thus, none of this series of reactions, in which the mercurated acylal is readily decomposed into the original reactants - the vinyl ether and the mercury salt - and so behaves as a typical complex compound, permits the question of the structure of the compounds to be resolved unequivocally. A decisive reaction for determining whether the mercurated acylals are addition products of mercury salt and vinyl ether or are complexes was found in the bromination reaction.

If the mercurated acylals are complexes of the type $(CH_3COO)_2Hg \cdot CH_2 = CHOR$, then bromination should give the known dibromides of vinyl ethers:

$$(CH_3COO)_2Hg \cdot CH_2 = CHOR + Br_2 \rightarrow BrCH_2CH(OR)Br + (CH_3COO)_2Hg.$$

If, however, they are not complexes, but products of the addition of mercury salts to the double bonds of vinyl ethers, then bromination should result in the formation of bromicated acylals:

$$CH_3 \cdot COOHgCH_2CH(OR)OCOCH_3 + Br_2 \rightarrow BrCH_2CH(OR)OCOCH_3 + CH_3COOHgBr.$$

When the bromination of the mercurated acylals was carried out, it was found that the products were not dibromides of vinyl ethers, but bromo acylals. Bromo acylals are rather unstable compounds, which decompose rapidly when kept or when heated slightly.

The general chemical behavior of mercurated acylals enables us to conclude that we have here a new example of the phenomenon, extensively studied in recent times, of dual reactivity in organic compounds arising from the σ-conjugation of bonds [11].

EXPERIMENTAL

Preparation of the Acetic Ester of Acetoxymercuriacetaldehyde Ethyl Hemiacetal. A mixture of 3.2 g (0.01 mole) of mercuric acetate and 10 ml of absolute ether was cooled, and 0.72 g (0.01 mole) of ethyl vinyl ether was added. The mercuric acetate dissolved rapidly. When the reaction mixture was cooled with ice and salt, the acetic ester of acetoxymercuriacetaldehyde ethyl hemiacetal, m.p. 38-39° (from ether), was precipitated. The yield was 3.6 g (92.3%).

Found %: C 24.28; 23.94; H 3.78; 3.64; Hg 51.90; 51.89
$CH_3COOHgCH_2CH(OC_2H_5)OCOCH_3$. Calculated %: C 24.61; H 3.59; Hg 51.44

Preparation of the Acetic Ester of Acetoxymercuriacetaldehyde Methyl Hemiacetal. A mixture of 6.4 g (0.02 mole) of mercuric acetate and 20 ml of absolute ether was cooled with ice and salt, and 4 ml of methyl vinyl ether was added. The yield of the acetic ester of acetoxymercuriacetaldehyde methyl hemiacetal was 7 g (91.7%); m.p. 48-49° (from acetone).

Found %: Hg 53.84
$CH_3COOHgCH_2CH(OCH_3)OCOCH_3$. Calculated %: Hg 53.28

Preparation of the Acetic Esters of Acetoxymercuriacetaldehyde Isopropyl and Butyl Hemiacetals. Isopropyl vinyl ether (0.86 g, i.e. 0.01 mole) was added with cooling to 3.2 g (0.01 mole) of mercuric acetate. The resulting oil was exposed to a vacuum for one hour to remove traces of isopropyl vinyl ether. The yield of the acetic ester of acetoxymercuriacetaldehyde isopropyl hemiacetal was 4 g (quantitative).

Found %: Hg 49.63; 49.75
$CH_3COOHgCH_2CH(OC_3H_7)OCOCH_3$. Calculated %: Hg 49.60

In a similar way, reaction of mercuric acetate with butyl vinyl ether gave a quantitative yield of the acetic ester of acetoxymercuriacetaldehyde butyl hemiacetal.

Found %: Hg 48.19; 48.40
$CH_3COOHgCH_2CH(OC_4H_9)OCOCH_3$. Calculated %: Hg 47.92

Preparation of the Acetic Ester of Acetoxymercuriacetaldehyde Phenyl Hemiacetal. To a cooled suspension of 3.2 g (0.01 mole) of mercuric acetate in 10 ml of dry acetone, 1.2 g (0.01 mole) of phenyl vinyl ether was added. When dissolution of the mercury salt was complete, the reaction mixture was cooled with ice and salt. The crystals of the acetic ester of acetoxymercuriacetaldehyde phenyl hemiacetal were filtered off; yield 4 g (93.1%); m.p. 96-97° (from ether).

Found %: Hg 45.95; 46.07
$CH_3COOHgCH_2CH(OC_6H_5)OCOCH_3$. Calculated %: Hg 45.73

Hydrolysis of the Acetic Ester of Acetoxymercuriacetaldehyde Ethyl Hemiacetal. A solution of 0.75 g (0.01 mole) of potassium chloride in 5 ml of water was added to a solution of 3.9 g (0.01 mole) of the acetic ester of acetoxymercuriacetaldehyde ethyl hemiacetal in 10 ml of water. The crystals of chloromercuriacetaldehyde were filtered off; yield 2.8 g (quantitative); m.p. 128-129° (from water). There was no depression in a mixture melting point test with chloromercuriacetaldehyde prepared from ethyl vinyl ether.

Found %: Hg 71.95; 72.22
$CHgCH_2CHO$. Calculated %: Hg 71.88

Reaction of the Acetic Ester of Acetoxymercuriacetaldehyde Ethyl Hemiacetal with Sodium Iodide. A mixture of 36 g (0.24 mole) of sodium iodide and 100 ml of dry cyclohexanone was cooled with ice and salt, and a solution of 23.4 g (0.06 mole) of the acetic ester of acetoxymercuriacetaldehyde ethyl hemiacetal in 15 ml of dry cyclohexanone was added. The mixture immediately became very thick. A fraction of boiling point 35-36°, amounting to 2.1 g (48.6%), was distilled from the reaction mixture on a water bath. The product (ethyl vinyl ether) had the following constants: b.p. 35-36°; n_D^{20} 1.3775; d_4^{20} 0.7545; found MR 21.97; calculated MR 21.85.

The literature [12] gives b.p. 36-36.1°; n_D^{20} 1.3779; d_4^{20} 0.7531. The ethyl vinyl ether obtained in this reaction was converted quantitatively into chloromercuriacetaldehyde [13].

Reaction of the Acetic Ester of Acetoxymercuriacetaldehyde Ethyl Hemiacetal with Acetyl Chloride. Acetyl chloride (2.2 ml, i.e. 0.03 mole) was added cautiously to a solution of 12 g (0.03 mole) of the acetic ester of acetoxymercuriacetaldehyde ethyl hemiacetal in 10 ml of absolute ether. The reaction mixture became noticeably warm. Ether was distilled off from a water bath. Vacuum distillation gave a fraction of b.p. 35-36° (10 mm), which was found to be acetic anhydride; yield 1.7 g (56.6%). A light-brown viscous mass remained in the distillation flask (ethyl vinyl ether polymer). After being redistilled, the acetic anhydride had the following constants: b.p. 36° (10 mm); n_D^{20} 1.3895; d_4^{20} 1.0779; found MR 22.43; calculated MR 22.34. The acetic anhydride was converted into acetanilide.

Reaction of the Acetic Ester of Acetoxymercuriacetaldehyde Ethyl Hemiacetal with Triethyl Phosphite. Triethyl phosphite (11.7 g, i.e. 0.07 mole) was added to the acetic ester of acetoxymercuriacetaldehyde ethyl hemiacetal (27.3 g, i.e. 0.07 mole). The reaction mixture became appreciably warm, and mercury separated immediately. The mixture was distilled from a water bath. The first fraction, b.p. 35-36°, was ethyl vinyl ether, obtained in 70% yield (3.5 g); n_D^{20} 1.3782; d_4^{20} 0.7564; found MR 21.98; calculated MR 21.85. A second fraction, b.p. 75-78°, yielded ethyl acetate in 86.0% yield (8.2 g); b.p. 76-77°; n_D^{20} 1.3733; d_4^{20} 0.9016; found MR 22.25; calculated MR 22.32. The literature [14] gives: b.p. 77.1°; n_D^{20} 1.3728; d_4^{20} 0.901.

Reaction of Triethyl Phosphite with Mercuric Acetate. To 16 g (0.05 mole) of mercuric acetate, 8.3 g (0.05 mole) of triethyl phosphite was added. Mercury separated rapidly, and the reaction mixture became very hot. When reaction was complete, a fraction boiling at 74-78° was distilled off; yield 4.8 g (54.5%). Redistillation yielded ethyl acetate having the following constants: b.p. 76-77°; n_4^{20} 1.3735 d_4^{20} ..8974; found MR 22.33; calculated MR 22.32.

Bromination of Mercurated Acylals. A solution of 2.5 ml (0.05 mole) of bromine in 10 ml of dry carbon tetrachloride was slowly added dropwise to a cooled (ice and salt) stirred solution of 19.5 g (0.05 mole) of the acetic ester of acetoxymercuriacetaldehyde ethyl hemiacetal in 50 ml of carbon tetrachloride. When the whole of the bromine had been added, the mixture was stirred for a few minutes further. The precipitate was filtered off and washed with dry carbon tetrachloride. Solvent was distilled from the filtrate, and the residue was distilled under reduced pressure. The acetic ester of bromoacetaldehyde ethyl hemiacetal came over at 77-79° (15 mm), the yield being 5.7 g (54%); it had n_D^{20} 1.4415; d_4^{20} 1.3610; found MR 40.38; calculated MR 40.97.

Found %: C 34.10; H 5.45

$BrCH_2CH(OC_2H_5)OCOCH_3$. Calculated %: C 34.12; H 5.21

The bromination of 40.4 g (0.1 mole) of the acetic ester of acetoxymercuriacetaldehyde isopropyl hemiacetal was carried out under similar conditions and gave 12.5 g (55.8%) of the acetic ester of bromoacetaldehyde isopropyl hemiacetal, b.p. 58° (5 mm); n_D^{20} 1.4457; d_4^{20} 1.3240; found MR 45.31; calculated MR 45.58.

Found %: C 37.29; 37.96; H 5.82; 6.09

$BrCH_2CH(OC_3H_7)OCOCH_3$. Calculated %: C 37.35; H 5.82

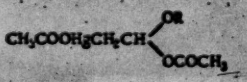
The bromination of 41.6 g (0.01 mole) of the acetic ester of acetoxymercuriacetaldehyde butyl hemiacetal yielded the acetic ester of bromoacetaldehyde butyl hemiacetal in 43.5% yield (10.4 g); this had b.p. 69-72° (5 mm); n_D^{20} 1.4445; d_4^{20} 1.2872; found MR 49.38; calculated MR 50.02.

Found %: C 40.11; 40.30; H 6.40; 6.44

$BrCH_2CH(OC_4H_9)OCOCH_3$. Calculated %: C 40.18; H 6.32

SUMMARY

1. By the addition of mercuric acetate to vinyl ethers, mercurated acylals of the following general formula were prepared:

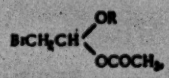


R = CH_3, C_2H_5, i-C_3H_7, C_4H_9, C_5H_9.

2. By an investigation of the chemical behavior of the mercurated acylals it was established that they

have dual reactivity.

3. Bromo acylals of the following formula were synthesized:



R = C_2H_5, i-C_3H_7, C_4H_9.

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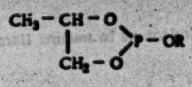
PROPERTIES AND REACTIONS OF ALKYL AND ARYL PROPYLENE PHOSPHITES

COMMUNICATION 1. ADDITION REACTIONS

A.E. Arbuzov and N.A. Razumova

Cyclic phosphorous esters were first synthesized and studied by A.E. Arbuzov and Zoroastrova in 1945 [1]. Later, similar compounds were studied by A.E. Arbuzov in collaboration with Rizpolozhensky [2] and Azanovskaya [3]. Some investigations in this direction were carried out by Kabachnik and Rossiiskaya [4]. Lucas and coworkers [5] prepared some esters of propylene hydrogen phosphite. The study of these cyclic esters by A.E. Arbuzov and coworkers has shown that the cyclic phosphorous esters are in many respects similar in properties to open-chain phosphorous esters, but they show differences in certain properties [1,2].

In order to make a further study of the reactions of cyclic phosphorous esters, we prepared some alkyl and aryl propylene phosphites, of which some have already been reported in the literature and some were synthesized for the first time. These esters are of formula



R = CH_3; C_2H_5; n-C_3H_7; i-C_3H_7; n-C_4H_9; i-C_4H_9; n-C_5H_{11}; n-C_7H_{15}; n-C_9H_{19}; C_6H_5.

Esters of propylene hydrogen phosphite were first prepared by Lucas and coworkers [5]; Lucas did not study their reactions. The constants of some of our esters were identical with the values found by Lucas. The last four compounds were synthesized by us for the first time, and their constants are given in Table 1.

The esters were prepared either by the action of alkyl phosphorodichloridites on 1,2-propanediol or by the action of an alcohol on propylene phosphorochloridite in presence of pyridine. Propylene phosphorochloridite was converted also into propylene hydrogen phosphite, the constants of which are given in Table 1 since this substance was not characterized by Lucas.

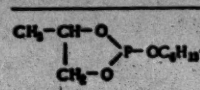
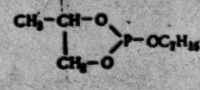
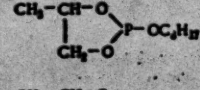
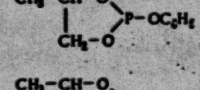
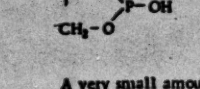
One of the characteristic reactions of compounds containing tervalent phosphorus is the addition of sulfur. It was found that sulfur adds to alkyl propylene phosphites with evolution of heat. Thus, in the addition of sulfur to 8 g of methyl propylene phosphite, the temperature rose from 18° to 206°. With increase in the size of the alkyl radical, the addition reaction becomes less vigorous and the rise in temperature is reduced correspondingly.

By addition of sulfur to alkyl propylene phosphites, some mixed esters of phosphorothionic acid were obtained. Their constants are given in Table 2.

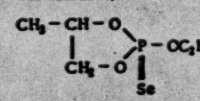
These phosphorothionic esters are colorless liquids. The methyl compound has an unpleasant thiol odor, but with increase in the size of the alkyl radical the odor becomes more feeble, and the hexyl compound is almost odorless.

A similar reaction - the addition of selenium - was carried out with ethyl propylene phosphite. Although the addition of selenium proceeds with evolution of heat, the selenium did not all react even when the mixture was heated to 130°. When the product was distilled in a high vacuum, it decomposed almost completely with separation of selenium.

TABLE 1

Formula of substance	B.p. in °C (p in mm)	d_4^0	d_4^{20}	n_D^{20}	MR		Analysis for P (%)	
					calculated	found	calculated	found
	109.5-111(15)	1.0369	1.0190	1.4465	54.62	54.0	15.05	15.03 14.96
	130-132(16)	1.0140	0.9974	1.4468	59.24	58.82	14.09	13.89 13.83
	134-135(10)	1.0031	0.9858	1.4470	63.86	63.56	13.25	13.23 13.47
	121-121.5(11)	1.2010	1.1820	1.5201	51.03	50.91	15.66	15.60 15.75
	96.5-97.5(1)	–	–	1.4705	–	–	25.40	25.03 25.04

A very small amount of an analytically pure mixed ester of phosphoroselenonic acid of the following formula was obtained:

 b.p. 107° (0.25 mm); n_D^{20} 1.4923

It was found that cuprous salts readily add to esters of propylene hydrogen phosphite with evolution of much heat, but no crystalline products were isolated. Some interesting reactions of these esters will be described in our second communication.

EXPERIMENTAL

Synthesis of Hexyl Propylene Phosphite

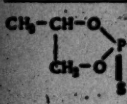
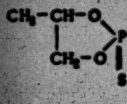
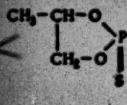
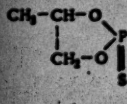
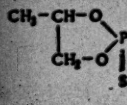
A mixture of 36.5 g of hexyl alcohol, 22 g of pyridine, and 1000 ml of absolute ether was prepared in a two-liter three-necked flask fitted with stirrer, dropping funnel, thermometer, and reflux condenser protected by a calcium chloride tube. The contents of the flask were vigorously stirred and cooled externally with snow and salt, and 50 g of propylene phosphorochloridite was added at such a rate that the temperature in the flask did not rise above −5°. When the whole of the acid chloride had been added, cooling was discontinued, but stirring was continued for 90 minutes at room temperature. The precipitate of pyridine hydrochloride was filtered off through a Nutsch filter and was washed 3-4 times on the filter with dry ether. After removal of ether the residue was vacuum-fractionated. Two fractionations (firstly with a Widmer column, and then from an Arbuzov flask) resulted in the isolation of the required hexyl ester, b.p. 109.5-111° (15 mm), in 19% yield (14 g); d_4^0 1.0369; d_4^{20} 1.0190; n_D^{20} 1.4465; found MR 54.00; calculated MR 54.62.

Found % P 15.03; 14.96

$C_9H_{19}O_3P$. Calculated % P 15.05

This ester is a colorless liquid of characteristic odor. It is sparingly soluble in organic solvents.

TABLE 8

Formula of substance	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Analysis for P (%) calculated	found
	130-138 (2.5)	1.3001	1.4930	18.45	18.36 18.38
	102-104 (0.5)	1.2072	1.4762	17.03	17.14 17.02
	99-101 (0.2)	1.1221	1.4662	15.88	15.82 16.00
	86.5-88 (0.12)	1.1232	1.4705	14.76	14.63 14.50
	118.5-119 (0.15)	1.0891	1.4725	13.83	12.95 13.16

Synthesis of Heptyl Propylene Phosphite

The same procedure was used in the preparation of heptyl propylene phosphite. Reaction between 57.1 g of the acid chloride, 47.1 g of heptyl alcohol, and 32.1 g of pyridine in 800 ml of ether yielded 27 g (29%) of the heptyl ester, b.p. 130-132° (16 mm).

Found %: P 14.09; 13.83

$C_{10}H_{21}O_3P$. Calculated %: P 14.09

The heptyl ester is a colorless liquid of characteristic odor. It is sparingly soluble in organic solvents.

Synthesis of Octyl Propylene Phosphite

A similar procedure was used. Reaction was between 74 g of propylene phosphorochloridite, 89 g of octyl alcohol, and 42 g of pyridine in 800 ml of dry ether. Two fractionations with a Widmer column resulted in the isolation of 51 g (43%) of octyl propylene phosphite, b.p. 134-135° (10 mm); d_4^{20} 1.0031; d_4^{20} 0.9858; n_D^{20} 1.4470.

Found %: P 13.47; 13.23

$C_{11}H_{23}O_3P$. Calculated %: P 13.25

This ester is a colorless liquid having a feeble, but unpleasant odor. It is sparingly soluble in organic solvents.

Synthesis of Phenyl Propylene Phosphite

Under similar conditions, 40.65 g of 1,2-propanediol reacted with the corresponding amount of phenyl phosphorodichloridite in presence of pyridine and yielded, after vacuum fractionation, 54 g (52%) of phenyl propylene phosphite, b.p. 121-121.5° (11 mm).

Found %: P 15.60; 15.75

$C_9H_{11}O_3P$. Calculated %: P 15.66

This ester is a colorless liquid of feeble odor. It is soluble in organic solvents.

Preparation of Propylene Hydrogen Phosphite

Propylene phosphorochloridite (22 g) was placed in an Arbuzov flask fitted with a dropping funnel. The flask was cooled with snow and ice at −20°. The calculated amount of water (2.82 g) was added very cautiously from the dropping funnel. The reaction was very violent at first, but later became quieter. By the end of the reaction the liquid had become very viscous. The hydrogen chloride formed in the reaction was removed with a vacuum pump. Two fractionations from the Arbuzov flask yielded 15.5 g (86%) of propylene hydrogen phosphite, b.p. 96.5-97.5° (1 mm). Owing to the high viscosity of the substance, its density was not determined; it had n_D^{20} 1.4705.

Found %: P 25.03; 25.04

$C_3H_7O_3P$. Calculated %: P 25.40

The acid ester is a very hygroscopic thick colorless liquid. It is readily soluble in water, alcohol, benzene, and toluene, and it is sparingly soluble in carbon tetrachloride, ether, and dichloroethane.

Reaction of Sulfur with Methyl Propylene Phosphite

A mixture of 8.1 g of methyl propylene phosphite and 1.9 g of sulfur was prepared in a round-bottomed two-necked flask fitted with thermometer and reflux condenser protected from moisture with a calcium chloride tube. The temperature in the flask was maintained at 40° for 3-4 minutes, but it then began to rise rapidly, attaining 205°. The liquid remained clear, but acquired a bright-yellow color; the whole of the sulfur dissolved. Two fractionations from an Arbuzov flask yielded O-methyl O,O-propylene phosphorothioate in 18% yield (1.8 g); it had b.p. 136-138° (2.5 mm); d_4^{20} 1.3182; d_4^{20} 1.3001; n_D^{20} 1.4930; found MR 37.56; calculated MR 37.47.

Found %: P 18.36; 18.35

$C_4H_9O_2PS$. Calculated %: P 18.45

This substance is a colorless mobile liquid having a powerful thiol odor. It is vigorously oxidized by concentrated nitric acid. It is sparingly soluble in organic solvents.

By the method described sulfur-addition products were prepared from ethyl, propyl, isobutyl, and hexyl propylene phosphites (Table 2).

Reaction of Selenium with Ethyl Propylene Phosphite

By reaction of 10.7 g of ethyl propylene phosphite with 5.9 g of selenium, a very small amount of O-ethyl O,O-propylene phosphorselenoate was obtained (0.7 g, i.e. 4.7%); it had b.p. 107° (0.125 mm); n_D^{20} 1.4923. It is a clear colorless liquid having a very unpleasant odor. When the substance is stored, the red modification of selenium separates.

Found %: P 13.72; 13.85

$C_5H_{11}O_3PSe$. Calculated %: P 13.54

SUMMARY

1. Some previously undescribed alkyl and aryl propylene phosphites have been synthesized.

2. It has been shown that alkyl propylene phosphites give addition reactions with sulfur, selenium, and cuprous halides.

3. Previously undescribed O-alkyl O-propylene phosphorothioates have been synthesized.

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[2] A.E. Arbuzov, V.M. Zoroastrova, and N.I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 208 (1948).

[3] A.E. Arbuzov and M.M. Azanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 473 (1949); 544 (1951).

[4] P.A. Rossiiskaya and M.I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 509 (1947).

[5] H.J. Lucas, F. Mitchell and C. Scully, J. Am. Chem. Soc., 72, 5491, 5779 (1950).

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*T.p. = C.B. Translation pagination

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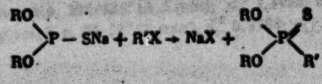
O,O- AND O,S-DIALKYL ALKYLPHOSPHONOTHIOATES

M.I. Kabachnik, T.A. Mastryukova, and N.I. Kurochkin

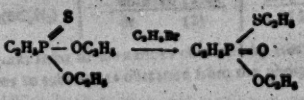
In a study of the properties of O,O-dialkyl hydrogen phosphorothioites, Kabachnik and Mastryukova [1] found that, when treated with alkyl halides, their sodium derivatives enter into a reaction similar to the well known reaction of Michaelis and Becker [2] with formation of O,O-dialkyl alkylphosphonothioates:



In the examples of the reaction studied, sodium O,O-diethyl phosphorothioite was alkylated with ethyl iodide, ethyl chloride, benzyl chloride, and ethyl chloroacetate.

The structure of the resulting alkylphosphonothioic esters was proved by hydrolyzing them to the corresponding alkylphosphonic acids. Alkylphosphonothioic esters have been prepared also by other investigators. Thus, Pudovik and Zametaeva [3] prepared O,O-dialkyl alkylphosphonothioates containing electronegative substituents in the p-alkyl by addition of O,O-dialkyl hydrogen phosphorothioites to suitable unsaturated compounds. Arbuzov and Rizpolozhensky [4] and Razumov, Mukhacheva, and Sim-Do-Ken [5] prepared some O,O--dialkyl alkylphosphonothioates by addition of sulfur to alkylphosphonous esters and by reaction of alkylphosphonous dichlorides with sulfur and subsequent conversion of the alkylphosphonothioic dichloride into the ester. Finally, Pudovik and Kavyrzina [6] have recently made use of our method for the synthesis of O,O-dialkyl alkylphosphonothioates, and starting from O,O-dibutyl hydrogen phosphorothioite they have prepared some O,O--dibutyl alkylphosphonothioates.

Of all the proposed methods for the synthesis of O,O-esters of simple alkylphosphonothioic acids, the most general and convenient from the preparative point of view is the synthesis that we have described, which is based on a reaction of the Michaelis-Becker type. In our paper we showed also that O,O-diethyl ethylphosphonothioate is able to undergo isomerization; when this ester is heated at 140-150° with ethyl iodide in a sealed tube for three hours, an isomeric ester is formed, and the product has a higher boiling point, density, and refractive index than the original ester. As is well known, such a change in physical constants is characteristic for the Pishchimuka rearrangement. We therefore concluded that a rearrangement of this type occurs when a phosphonothionic ester is heated with an alkyl halide:



At that time we did not carry out a more rigorous proof of the structure of the ester obtained. In the present investigation we synthesized various O,O-dialkyl alkylphosphonothioates by the method described by us previously. In all cases the reaction gave the required product in satisfactory yields, ranging from 25% to 65%. The constants of the resulting esters are given in Table 1.

All of the phosphonothionic esters so obtained were subjected to the Pishchimuka rearrangement, for

which purpose they were heated with the corresponding alkyl bromides in sealed tubes at 140-200° for 4-10 hours. The higher the molecular weight of the ester, the more severe were the conditions required for reaction. The resulting phosphonthiolic esters were found to be colorless liquids of characteristic odor. Table 2 gives the physical constants of the phosphonothiolic esters (O,S-dialkyl alkylphosphonothioates) that we prepared.

TABLE 1

No.	Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated
1	$CH_3PS(OC_2H_5)_2$	76.5-78 (13)	1.4610	1.0553	43.73	43.64
2	$C_2H_5PS(OC_2H_5)_2$ *	80-83 (10)	1.4576	1.0324	48.12	48.26
3	$C_3H_7PS(OC_2H_5)_2$	83.5-85.5 (2)	1.4598	1.0158	52.86	52.88
4	$C_4H_9PS(OC_2H_5)_2$	74.5-77.5 (2.5)	1.4600	1.0004	57.57	57.50
5	$C_6H_5CH_2PS(OC_2H_5)_2$ **	125.5-127.5 (3)	1.5305	1.1031	68.46	67.75
6	$CH_3PS(OC_4H_9)_2$	72-74 (1)	1.4535	0.9848	61.62	62.12
7	$C_2H_5PS(OC_4H_9)_2$ ***	79.5-83 (2)	1.4533	0.9775	65.94	66.74

*The literature gives: b.p. 90-93.5° (13 mm); d_4^{20} 1.0324; n_D^{20} 1.4545 [1].
**The literature gives: b.p. 124-125° (3.5 mm); d_4^{25} 1.1022; n_D^{20} 1.5303 [1].
***The literature gives: b.p. 97-98° (2 mm); d_4^{20} 0.9768; n_D^{20} 1.4510 [6].

TABLE 2

No.	Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated
8	$CH_3PO(OC_2H_5)(SC_2H_5)$	106-108.5 (18)	1.4718	1.0904	43.18	43.35
9	$C_2H_5PO(OC_2H_5)(SC_2H_5)$*	66.5-68 (2.5)	1.4747	1.0670	48.08	47.97
10	$C_3H_7PO(OC_2H_5)(SC_2H_5)$	85-86.5 (3)	1.4733	1.0447	52.63	52.59
11	$C_4H_9PO(OC_2H_5)(SC_2H_5)$	98.5-100 (2.5)	1.4728	1.0262	57.46	57.12
12	$C_6H_5CH_2PO(OC_2H_5)(SC_2H_5)$	134-136 (2)	1.5350	1.1263	67.52	67.46
13	$CH_3PO(OC_4H_9)(SC_4H_9)$	102-104.5 (1.5)	1.4664	1.0068	61.75	61.93
14	$C_2H_5PO(OC_4H_9)(SC_4H_9)$	92-94 (2)	1.4660	0.9951	66.33	66.45

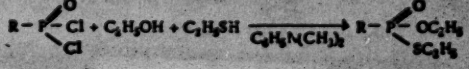
*The literature gives: b.p. 76-76.5° (4 mm); d_4^{20} 1.0709; n_D^{20} 1.4730 [1].

TABLE 3

Formula of substance	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}
$CH_3PO(OC_2H_5)(SC_2H_5)$	106-108.5* (18)	1.0904	1.4718
	110-111 (22)	1.0940	1.4743
$C_2H_5PO(OC_2H_5)(SC_2H_5)$	66.5-68 (2.5)	1.0670	1.4747
	64 (2)	1.0717	1.4721

*The upper figures refer to substances obtained by isomerization, and the lower figures to substances obtained from the phosphonic dichloride.

In order to prove the structure of the isomerization products, we took O,S-diethyl methyl- and ethyl-phosphonothioates as examples. We synthesized these substances by a method that left no doubt regarding their structure, namely by reaction between methylphosphonic dichloride, ethanol, and ethanethiol:



The properties and constants of the substances prepared by the two methods were practically identical (Table 3).

Moreover, the infrared spectra of the isomeric diethyl and dibutyl alkylphosphonothioates (Nos. 1-7 and Nos. 8-14) show quite clearly that the first are thionic isomers, and the second thiolic isomers (the presence of an intense absorption band in the region of 1215 cm^{-1} in the spectra of the latter is characteristic for substances containing a P=O linkage [7]).

EXPERIMENTAL

Preparation of O,O-Dialkyl Alkylphosphonothioates

The O,O-dialkyl hydrogen phosphorothiolte was converted into its sodium derivative by treatment with the calculated amount of sodium ethoxide, and the alkyl halide was then added dropwise with cooling. The reaction mixture was stirred at 70-80° for 2-3 hours, when the reaction mixture was found to be only weakly alkaline. The resulting sodium halide, which formed in a colloidal condition, was coagulated by adding a few drops of water and then heating the mixture. The sodium halide was filtered off, and the filtrate was dried over sodium sulfate. Benzene and alcohol were distilled off, and the residue was vacuum-distilled. Yields of 25-65% were obtained.

O,O-Diethyl Methylphosphonothioate. This was prepared from 15.4 g (0.1 mole) of O,O-diethyl hydrogen phosphorothiolte, sodium ethoxide prepared from 2.25 g (0.1 mole) of sodium and 4.5 g (0.1 mole) of dry ethanol, and 14.5 g (0.1 mole) of methyl iodide. The product, obtained in 42% yield (6.8 g) had b.p. 76.5-78° (13 mm); n_D^{18} 1.4610; d_4^{20} 1.0553; found MR 43.73, calculated MR 43.84.

Found %: C 36.28; 36.23; H 8.14; 8.05; P 18.68; 18.34
$C_5H_{13}O_2PS$. Calculated %: C 35.70; H 7.79; P 18.42

O,O-Diethyl Ethylphosphonothioate. This was prepared from 20 g (0.13 mole) of O,O-diethyl hydrogen phosphorothiolte, 8.8 g (0.13 mole) of sodium ethoxide, and 15 g (0.14 mole) of ethyl bromide. The product, amounting to 11.4 g (46%), had b.p. 80-83° (10 mm); n_D^{20} 1.4576; d_4^{20} 1.0324*.

O,O-Diethyl Propylphosphonothioate. This was prepared from 20 g (0.13 mole) of O,O-diethyl hydrogen phosphorothiolte, sodium ethoxide prepared from 3.0 g (0.13 mole) of sodium and 6.0 g (0.13 mole) of dry ethanol, and 16.0 g (0.13 mole) of propyl bromide. The product, amounting to 6 g (24%), had b.p. 63.5-65.5° (2 mm); n_D^{19} 1.4590; d_4^{20} 1.0158; found MR 52.86; calculated MR 52.88.

Found %: C 43.09; 42.94; H 8.86; 8.74; P 15.57; 15.95
$C_7H_{17}O_2PS$. Calculated %: C 42.82; H 8.73; P 15.77

O,O-Diethyl Butylphosphonothioate. This was prepared from 20.0 g (0.13 mole) of O,O-diethyl hydrogen phosphorothiolte, 8.8 g (0.13 mole) of sodium ethoxide, and 18.0 g (0.13 mole) of butyl bromide. The product amounting to 12.7 g (46%), had b.p. 74.5-77.5° (2.5 mm); n_D^{20} 1.4600; d_4^{20} 1.0004; found MR 57.57; calculated MR 57.50.

Found %: C 45.78; 45.93; H 9.20; 9.23; P 14.39; 14.60
$C_8H_{19}O_2PS$. Calculated %: C 45.67. H 9.10; P 14.73

O,O-Diethyl Benzylphosphonothioate. This was prepared from 16.5 g (0.11 mole) of O,O-diethyl hydrogen phosphorothiolte, 7.5 g (0.11 mole) of sodium ethoxide prepared from 5.05 g (0.11 mole) of dry ethanol and 2.5 g (0.11 mole) of sodium, and 13.9 g (0.11 mole) of benzyl chloride. It was obtained in 34% yield (8.8 g) and had b.p. 125.5-127.5° (3 mm); n_D^{18} 1.5305; d_4^{20} 1.1031; found MR 68.46; calculated MR 67.76.

Found %: C 54.65; 54.52; H 7.10; 6.93; P 12.64; 12.72
$C_{11}H_{17}O_2PS$. Calculated %: C 54.08; H 7.01; P 12.68

O,O-Dibutyl Methylphosphonothioate. This was prepared from 30 g (0.14 mole) of O,O-dibutyl hydrogen phosphorothiolte, sodium ethoxide prepared from 3.2 g (0.14 mole) of sodium and 6.4 g (0.14 mole) of dry ethanol, and 25 g (0.16 mole) of methyl iodide. It was obtained in 41% yield (13.0 g) and had b.p. 72-74° (1 mm); n_D^{20} 1.4535; d_4^{20} 0.9848; found MR 61.62; calculated MR 62.12.

Found %: P 13.87; 14.01
$C_9H_{21}O_2PS$. Calculated %: P 13.82

*The literature gives b.p. 90-93.5° (13 mm); n_D^{20} 1.4545; d_4^{20} 1.0324.

O,O-Dibutyl Ethylphosphonothioate. This was prepared from 39 g (0.18 mole) of O,O-dibutyl hydrogen phosphorothioite, 6.2 g (0.18 mole) of sodium ethoxide, and 20.5 g (0.19 mole) of ethyl bromide. It was obtained in 65% yield (28 g) and had b.p. 79.5-83° (2 mm); n_D^{20} 1.4533; d_4^{20} 0.9775; found MR 65.94; calculated MR 66.74°.

Preparation of O,S-Dialkyl Alkylphosphonothioates

O,S-Dialkyl alkylphosphonothioates were prepared by the isomerization of O,O-dialkyl alkylphosphonothioates in presence of excess of alkyl halide in sealed tubes. The temperature and duration of heating, depending on the identity of the original ester, ranged from 140° to 200° and from 4 to 11 hours, respectively. When cool, the tube was opened, and its contents were transferred to a Claisen flask. Excess of alkyl halide and other readily volatile substances were distilled from the solution, and the residue was vacuum-distilled.

O,S-Diethyl Methylphosphonothioate. This was prepared from 5.4 g (0.03 mole) of O,O-diethyl methylphosphonothioate, which was heated at 140-150° for 10 hours with 10 g (0.09 mole) of ethyl bromide. It was obtained in 31% yield (1.7 g) and had b.p. 106-108.5° (18 mm); n_D^{20} 1.4718; d_4^{20} 1.0904; found MR 43.18; calculated MR 43.35.

Found %: C 35.12; 35.39; H 8.00; 7.82; P 18.25; 17.98
$C_5H_{13}O_2PS$. Calculated %: C 35.70; H 7.78; P 18.42

O,S-Diethyl Ethylphosphonothioate. This was prepared from 9.2 g (0.05 mole) of O,O-diethyl ethylphosphonothioate, which was heated at 155-165° for 4 hours with 25.4 g (0.23 mole) of ethyl bromide. It was obtained in 33% yield (3.0 g) and had b.p. 66.5-68° (2.5 mm); n_D^{20} 1.4747; d_4^{20} 1.0670**; found MR 48.06; calculated MR 47.97.

O,S-Diethyl Propylphosphonothioate. This was prepared from 5.6 g (0.03 mole) of O,O-diethyl propylphosphonothioate, which was heated at 190-200° for 4 hours with 3.1 g (0.028 mole) of ethyl bromide. It was obtained in 52% yield (2.9 g) and had b.p. 85-86.5° (3 mm); n_D^{20} 1.4733; d_4^{20} 1.0447; found MR 52.83; calculated MR 52.59.

Found %: C 42.67; 42.54; H 8.92; 8.85; P 16.15; 15.99
$C_7H_{17}O_2PS$. Calculated %: C 42.82; H 8.73; P 15.77

O,S-Diethyl Butylphosphonothioate. This was prepared from 10.8 g (0.05 mole) of O,O-diethyl butylphosphonothioate, which was heated at 180-190° for 6 hours with 11 g (0.1 mole) of ethyl bromide. It was obtained in 30% yield (3.2 g) and had b.p. 98.5-100°; n_D^{20} 1.4728; d_4^{20} 1.0262; found MR 57.46; calculated MR 57.12.

Found %: P 14.73; 14.79
$C_8H_{19}O_2PS$. Calculated %: P 14.73

O,S-Diethyl Benzylphosphonothioate. This was prepared from 8.4 g (0.033 mole) of O,O-diethyl benzylphosphonothioate, which was heated at 170-180° for 8 hours with 10 g (0.09 mole) of ethyl bromide. It was obtained in 42% yield (3.5 g) and had b.p. 134-136° (2 mm); n_D^{20} 1.5350; d_4^{20} 1.1263; found MR 67.52; calculated MR 67.46.

Found %: C 53.67; 53.91; H 7.07; 7.16; P 12.92; 13.02
$C_{11}H_{17}O_2PS$. Calculated %: C 54.08; H 7.01; P 12.68

O,S-Dibutyl Methylphosphorothioate. This was prepared from 6.8 g (0.03 mole) of O,O-dibutyl methylphosphonothioate, which was heated at 160-170° for 10 hours with 16.5 g (0.12 mole) of butyl bromide. It was obtained in 22% yield (1.5 g) and had b.p. 102-104.5° (1.5 mm); n_D^{20} 1.4664; d_4^{20} 1.0068; found MR 61.75; calculated MR 61.83.

Found %: C 48.13; 48.31; H 9.45; 9.44; P 13.77; 13.87
$C_9H_{21}O_2PS$. Calculated %: C 48.22; H 9.38; P 13.82

O,S-Dibutyl Ethylphosphonothioate. This was prepared from 16.3 g (0.07 mole) of O,O-dibutyl ethyl-

*The literature [6] gives b.p. 97-98° (2 mm); n_D^{20} 1.4510; d_4^{20} 0.9768.
**The literature [1] gives b.p. 76-76.5° (4 mm); n_D^{20} 1.4730; d_4^{20} 1.0709.

phosphonothioate, which was heated at 170-180° for 7 hours with 17 g (0.12 mole) of butyl bromide. It was obtained in 14% yield (2.2 g) and had b.p. 92-94° (2 mm); n_D^{18} 1.4600; d_4^{20} 0.9951; found MR 66.33; calculated MR 66.45.

Found %: P 12.59; 12.73
$C_{10}H_{23}O_2PS$. Calculated %: P 13.00

Synthesis of O,S-Diethyl Methylphosphonothioate

Dry ethanol (7.0 g, i.e. 0.15 mole) was added to a cooled mixture of 20 g (0.15 mole) of methylphosphonic dichloride, 19.4 g (0.16 mole) of dimethylaniline, and 150 ml of absolute ether. The reaction mixture was stirred at room temperature for three hours. The precipitate of dimethylaniline hydrochloride was then filtered off, and the filtrate was dried over calcined sodium sulfate. An ethereal solution of the ethyl methylphosphonochloridate so obtained was added to sodium mercaptide prepared from 6.2 g (0.1 mole) of ethanethiol and 2.3 g (0.1 mole) of sodium in 50 ml of dry ether. The reaction mixture became slightly warm. When the addition was complete, the mixture was set aside at room temperature for two days. The reaction mixture was treated with water, the ether layer was separated, and the aqueous layer was extracted with ether. The ether extracts were combined and dried over calcined sodium sulfate. After removal of ether and two vacuum distillations, 1.8 g of O,S-diethyl methylphosphonothioate was obtained; it had b.p. 110-111° (22 mm); d_4^{20} 1.0940; n_D^{18} 1.4743.

O,S-Diethyl Ethylphosphonothioate. This ester was prepared in a similar way from 24.6 g (0.16 mole) of ethylphosphonic dichloride; b.p. 64° (2 mm); d_4^{20} 1.0717; n_D^{18} 1.4721; yield 12.8 g (64%).

SUMMARY

1. Some O,O-dialkyl alkylphosphonothioates were prepared by a reaction of the Michaelis-Becker type.

2. It was found that when these esters were heated with alkyl halides to 140-200° Pishchimuka rearrangement occurred with formation of the isomeric O,S-dialkyl alkylphosphonothioates.

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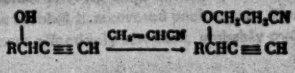
ACETYLENE DERIVATIVES

COMMUNICATION 173. CYANOETHYLATION OF ACETYLENIC ALCOHOLS

I.N. Nazarov and G.A. Shvekhgeimer

In previous papers [1] we have described the cyanoethylation of various acetylenic alcohols and glycols. Continuing this work, we have now studied the reaction of acrylonitrile with other secondary and tertiary acetylenic alcohols. The cyanoethylation reaction was carried out under comparable conditions at 20-30° for 20-24 hours, the catalyst being a 40% aqueous solution of potassium hydroxide.

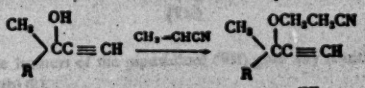
The secondary acetylenic alcohols - ethynylmethylmethanol (3-butyn-2-ol) and ethylethynylmethanol (1-pentyn-3-ol) - reacted very vigorously with acrylonitrile, being converted into the corresponding 2-cyanoethyl ethers (I) in 80-90% yield:



(I)

R = CH_3, C_2H_5

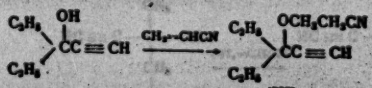
In the series of tertiary acetylenic alcohols, increase in the size of a straight-chain radical has no appreciable effect on the cyanoethylation reaction, the corresponding 2-cyanoethyl ethers (II) being obtained in more than 90% yield:



(II)

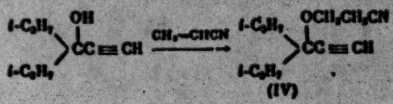
R = n-C_3H_7, n-C_5H_{11}, n-C_9H_{17}

In the cyanoethylation of diethylethynylmethanol (3-ethyl-1-pentyn-3-ol), the 2-cyanoethyl ether (III) was obtained in 94% yield:



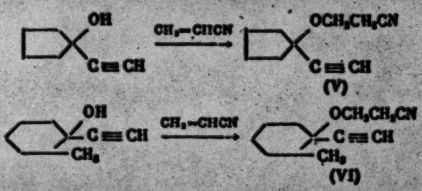
(III)

The cyanoethylation of tertiary acetylenic alcohols having branched chains was considerably more difficult. For example, in the cyanoethylation of ethynyldiisopropylmethanol (3-isopropyl-4-methyl-1-pentyn-3-ol), the 2-cyanoethyl ether (IV) was obtained in a yield of 97% on the amount of alcohol that reacted, but two-thirds of the acetylenic alcohol taken was recovered unchanged:



(IV)

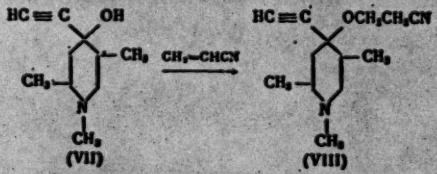
Acrylonitrile adds smoothly also to 1-ethynylcyclopentanol and to 1-ethynyl-2-methylcyclohexanol with formation of the 2-cyanoethyl ethers (V) and (VI) in yields of greater than 90%:



(V)

(VI)

The results of the cyanoethylation of two stereoisomers of 4-ethynyl-1,2,5-trimethylpiperidinol (VII) show the effect of the spatial structure of a molecule on the addition of acrylonitrile. The low-melting isomer of (VII), m.p. 109-110°, reacting in dioxane solution at 30-40°, forms the 2-cyanoethyl ether (VIII) in 93% yield, about two-fifths of the original alcohol being recovered unchanged. Under the same conditions, the high-melting isomer of (VII), m.p. 176-177°, reacts with acrylonitrile only with great difficulty, and almost the whole of the alcohol is recovered unchanged. Thus, the hydroxyl group in the high-melting piperidinol (VII) is much more effectively screened, probably owing to its cis position with respect to the neighboring methyl group.

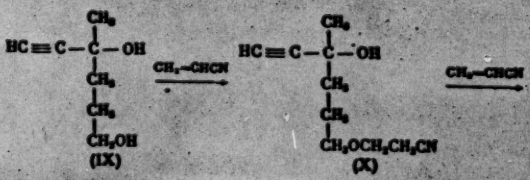


(VII)

(VIII)

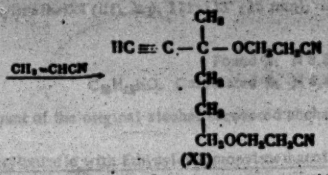
Neither of the isomers of the piperidinol (VII) give any reaction with acrylonitrile in absence of catalyst (caustic potash) [2].

Cyanoethylation of the acetylenic glycol (IX), which is prepared by the condensation of acetylene with 5-hydroxy-2-pentanone, proceeds in two stages. The first acrylonitrile molecule reacts with the primary hydroxyl with formation of the monocyanoethyl ether (X), which then combines with a second acrylonitrile molecule with formation of the bis-2-cyanoethyl ether (XI):



(IX)

(X)



(XI)

The postulated position of the 2-cyanoethyl group in the monocyanoethyl ether (X) was confirmed by its nonreaction with naphthyl isocyanate, i.e. with respect to this reagent it behaves as a tertiary acetylenic alcohol. The glycol (IX), which has a free primary hydroxyl, readily reacts with naphthyl isocyanate.

EXPERIMENTAL

Reaction of Acrylonitrile with Ethynylmethylmethanol

Acrylonitrile (8.5 g, i.e. 0.16 mole) was added to a vigorously stirred mixture of 11.2 g (0.16 mole) of ethynylmethylmethanol (b.p. 102-107°) and 1.5 g of a 40% aqueous solution of potassium hydroxide, the rate of addition being adjusted so that the temperature of the mixture did not exceed 30°. When the addition was complete, the mixture was stirred at room temperature for four hours. It was then set aside overnight, and on the next day the alkali present was neutralized with dilute hydrochloric acid (1:1). The product was extracted with ether and the extract was dried with magnesium sulfate. Vacuum fractionation yielded 15.4 g of the 2-cyanoethyl ether of ethynylmethylmethanol (I; R = CH_3), b.p. 94-96° (16 mm); n_D^{20} 1.4351; d_4^{20} 0.9450; found MR 33.97; calculated MR 33.92.

Found %: N 10.65; 10.71

C_7H_9NO. Calculated %: N 11.38

The amount of the original alcohol recovered unchanged was 0.7 g.

The cyanoethylation of the other acetylenic alcohols was carried out in the same manner.

Reaction of Acrylonitrile with Ethylethynylmethanol

Reaction was between 50.5 g (0.6 mole) of ethylethynylmethanol (b.p. 123-124°) and 32 g (0.6 mole) of acrylonitrile in presence of 6 g of 40% aqueous caustic potash. The product was 73.5 g of the 2-cyanoethyl ether of ethylethynylmethanol (I; R = C_2H_5), b.p. 104-105° (15 mm); n_D^{20} 1.4393; d_4^{20} 0.9357; found MR 38.53; calculated MR 38.54.

Found %: N 9.83; 9.75

$C_8H_{11}NO$. Calculated %: N 10.22

The amount of the original alcohol recovered unchanged was 1.8 g.

Reaction of Acrylonitrile with Ethynylmethylpropylmethanol

Reaction was between 56 g (0.5 mole) of ethynylmethylpropylmethanol (2-propyl-3-butyn-2-ol) (b.p. 136-137°) and 26.5 g (0.5 mole) of acrylonitrile in presence of 6 g of 40% aqueous caustic potash. The product was 61.7 g of the 2-cyanoethyl ether of ethynylmethylpropylmethanol (II; R = n-C_3H_7), b.p. 112-114° (15 mm); n_D^{20} 1.4416; d_4^{20} 0.9163; found MR 47.61; calculated MR 47.78

Found %: N 8.39; 8.42

$C_{10}H_{15}NO$. Calculated %: N 8.48

The amount of the original alcohol recovered unchanged was 9.1 g.

Reaction of Acrylonitrile with Diethylethynylmethanol

Reaction was between 56 g (0.5 mole) of diethylethynylmethanol (b.p. 135-136°) and 26.5 g (0.5 mole) of acrylonitrile in presence of 6 g of 40% aqueous caustic potash. The product was 69.5 g of the 2-cyanoethyl ether of diethylethynylmethanol (III), b.p. 111-113° (15 mm); n_D^{20} 1.4438; d_4^{20} 0.9228; found MR 47.49; calculated MR 47.78.

Found %: N 8.62; 8.50
$C_{11}H_{15}NO$. Calculated %: N 8.48

The amount of the original alcohol recovered unchanged was 6.1 g.

Reaction of Acrylonitrile with Ethynyldiisopropylmethanol

Reaction was between 45 g (0.32 mole) of ethynyldiisopropylmethanol (b.p. 164-165°) and 20 g (0.38 mole) of acrylonitrile in presence of 5 g of 40% aqueous caustic potash. The usual treatment yielded 20.2 g of the 2-cyanoethyl ether of ethynyldiisopropylmethanol (IV), b.p. 126-128° (13 mm); n_D^{20} 1.4490; d_4^{20} 0.9260; found MR 55.90; calculated MR 57.10.

Found %: N 7.41; 7.54
$C_{13}H_{21}NO$. Calculated %: N 7.25

The amount of the original alcohol recovered unchanged was 30.1 g.

Reaction of Acrylonitrile with Ethynylhexylmethylmethanol

Reaction was between 45 g (0.32 mole) of ethynyl hexylmethylmethanol (1-ethynyl-1-methyl-1-heptanol) (b.p. 94-95°/19 mm) and 21.5 g (0.4 mole) of acrylonitrile in presence of 7 g of 40% aqueous caustic potash. The mixture was stirred for four hours at room temperature, and was then set aside for 48 hours. The product was 72.4 g of the 2-cyanoethyl ether of ethynylhexylmethylmethanol (II; R = n-C_6H_{13}), b.p. 115-116° (2.5 mm); n_D^{20} 1.4442; d_4^{20} 0.8997; found MR 61.42; calculated MR 61.63.

Found %: N 6.78; 6.83
$C_{15}H_{25}NO$. Calculated %: N 6.76

The amount of the original alcohol recovered unchanged was 7.8 g.

Reaction of Acrylonitrile with Ethynylmethyloctylmethanol

Reaction was between 55 g (0.3 mole) of ethynylmethyloctylmethanol (1-ethynyl-1-methyl-1-nonanol) (b.p. 138°/19 mm) and 16 g (0.3 mole) of acrylonitrile in presence of 6 g of 40% aqueous caustic potash. The product was 66.2 g of the 2-cyanoethyl ether of ethynylmethyloctylmethanol (II; R = n-C_8H_{17}), b.p. 148-150° (3.5 mm); n_D^{20} 1.4498; d_4^{20} 0.8693; found MR 70.99; calculated MR 70.87.

Found %: N 5.82; 5.92
$C_{17}H_{29}NO$. Calculated %: N 6.00

The amount of the original alcohol recovered unchanged was 3.5 g.

Reaction of Acrylonitrile with 1-Ethynylcyclopentanol

Reaction was between 22 g (0.2 mole) of 1-ethynylcyclopentanol (b.p. 155-156°) and 11 g (0.2 mole) of acrylonitrile in presence of 3 g of 40% aqueous caustic potash. The product was 30.5 g of the 2-cyanoethyl ether of 1-ethynylcyclopentanol (V), b.p. 125-127° (14 mm); n_D^{20} 1.4684; d_4^{20} 0.9936; found MR 45.63; calculated MR 45.58.

Found %: C 73.10; 73.28; H 7.83; 7.83
$C_{10}H_{13}NO$. Calculated %: C 73.62; H 7.97

The amount of the original alcohol recovered unchanged was 1.5 g.

Reaction of Acrylonitrile with 1-Ethynyl-2-methylcyclohexanol

Reaction was between 49 g (0.355 mole) of 1-ethynyl-2-methylcyclohexanol (b.p. 57-58°/3 mm) and 21.2 g

(0.4 mole) of acrylonitrile in presence of 7 g of 40% aqueous caustic potash. The mixture was stirred for seven hours at room temperature and then set aside for 48 hours. The product was 56.6 g of the 2-cyanoethyl ether of 1-ethynyl-2-methylcyclohexanol (VI), b.p. 135-136° (10 mm); n_D^{15} 1.4710; d_4^{20} 0.9783; found MR 61.69; calculated MR 61.84.

Found %: N 7.79; 7.88
$C_{12}H_{17}NO$. Calculated %: N 7.89

The amount of the original alcohol recovered unchanged was 6.8 g.

Reaction of Acrylonitrile with 4-Ethynyl-1,2,5-trimethylpiperidinol

a) A mixture of 51 g (0.3 mole) of the low-melting isomer of 4-ethynyl-1,2,5-trimethylpiperidinol (VII) (m.p. 109-110°), 20 g (0.38 mole) of acrylonitrile, 6 g of 40% aqueous caustic potash, and 25 ml of dioxane was stirred at 30-40° for four hours and at room temperature for six hours; it was then set aside overnight. The product was 35.3 g of the 2-cyanotheyl ether of 4-ethynyl-1,2,5-trimethylpiperidinol (VIII), b.p. 135-137° (3 mm); n_D^{15} 1.4817; d_4^{15} 0.9943; found MR 63.04; calculated MR 63.37.

Found %: N 13.35; 13.29
$C_{13}H_{18}N_2O$. Calculated %: N 12.72

The amount of the original piperidinol recovered unchanged was 22.4 g.

b) A mixture of 17 g (0.1 mole) of the high-melting isomer of 4-ethynyl-1,2,5-trimethylpiperidinol (VII) (m.p. 176-177°), 8 g (0.15 mole) of acrylonitrile, 2 g of 40% aqueous caustic potash, and 50 ml of dioxane was stirred at 40-45° for eight hours and then set aside overnight. The product, amounting to 3.7 g, boiled at 110-130° (13 mm). The amount of the original piperidinol recovered unchanged was 13.8 g.

Reaction of Acrylonitrile with 4-Ethynyl-1,4-pentanediol

a) Reaction was between 10 g (0.08 mole) of the acetylenic glycol (IX) (b.p. 105-106°/2.5 mm) and 4.1 g (0.08 mole) of acrylonitrile in presence of 1.5 g of 40% aqueous caustic potash. The main product was 9.4 g of the 2-cyanoethyl ether (X), b.p. 148-150° (3 mm); n_D^{15} 1.4608; d_4^{20} 1.0231.

Found %: C 66.27; 66.09; H 7.99; 8.11
$C_{11}H_{15}NO_3$. Calculated %: C 66.30; H 8.28

The reaction also gave 3.2 g of the bis-2-cyanoethyl ether of 4-ethynyl-1,4-pentanediol (XI), b.p. 190-192° (3 mm); n_D^{15} 1.4801; d_4^{20} 1.0276.

Found %: N 12.22; 12.19
$C_{15}H_{18}N_2O_2$. Calculated %: N 11.96

b) Reaction was between 7.5 g (0.06 mole) of the acetylenic glycol (IX) and 6.4 g (0.12 mole) of acrylonitrile in presence of 2.5 g of 40% aqueous caustic potash. The main product was 7.4 g of the bis-2-cyanoethyl ether of 4-ethynyl-1,4-pentanediol (XI), b.p. 182-185° (3.5 mm). The reaction gave also 4.5 g of the 2-cyanoethyl ether (X), b.p. 153-156° (3.5 mm).

Reaction of Acrylonitrile with the 2-Cyanoethyl Ether (X)

Reaction was between 9 g (0.05 mole) of the 2-cyanoethyl ether (X) and 4.2 g (0.08 mole) of acrylonitrile in presence of 1.5 g of 40% aqueous caustic potash. The product was 6.9 g of the bis-2-cyanoethyl ether of 4-ethynyl-1,4-pentanediol (XI), b.p. 190-195° (3 mm), and 3.4 g of the original 2-cyanoethyl ether (X) was recovered unchanged.

SUMMARY

1. Some secondary and tertiary acetylenic alcohols were cyanoethylated in presence of caustic potash, and the corresponding 2-cyanoethyl ethers were obtained in good yield. In the case of ethynyldiisopropylmethanol the greater part of the original alcohol was recovered unchanged.

2. Of the two isomers of 4-ethynyl-1,2,5-trimethylpiperidinol (VII), only the low-melting isomer reacts with acrylonitrile and gives the corresponding 2-cyanoethyl ether (VIII). The high-melting isomer of this piper-

idinol does not react with acrylonitrile under the usual conditions.

3. The acetylenic glycol (IX) reacts with acrylonitrile with formation of mono- and bis-2-cyanoethyl ethers, and the first acrylonitrile molecule reacts at the primary hydroxyl group.

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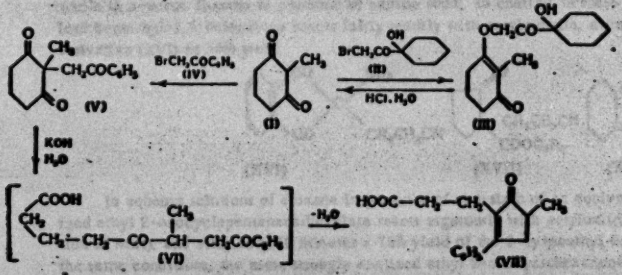
*T.p. = C.B. Translation pagination

EFFECT OF ENOLIZATION ON THE ABILITY OF β-DICARBONYL COMPOUNDS TO UNDERGO MICHAEL AND C-ALKYLATION REACTIONS

I.N. Nazarov, S.I. Zavylov, and M.S. Burmistrova

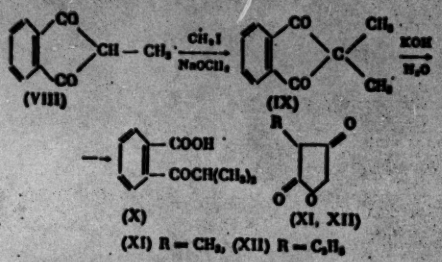
In a series of previous investigations [1-4] we have studied the condensation of dihydroresorcinol derivatives with various α,β-unsaturated carbonyl compounds, and on the basis of these reactions we have developed methods for the preparation of some bicyclic ketones that are of interest as intermediate products in the synthesis of polycyclic compounds related to steroids. The present communication presents new data on the alkylation and Michael condensation of cyclic β-diketones, and an examination is made of the dependence of the course of these reactions on the extent of enolization of the carbonyl compounds.

The dual reactivity of β-diketones in nucleophilic substitution reactions is greatly dependent on the structures of the reactants and the character of the solvent (medium); it is governed by very complex laws. We have now found, for example, that bromomethyl 1-hydroxycyclohexyl ketone (II) reacts when heated with the potassium derivative of 2-methyldihydroresorcinol (2-methyl-1,3-cyclohexanedione) in methanol solution with formation of the corresponding enol ether (III) in 40% yield, whereas 2-bromoacetophenone (IV), a substance of similar structure, reacts under these conditions with formation of the C-derivative (V) in 44% yield. When shaken in the cold with 2% hydrochloric acid, the enol ether (III) is hydrolyzed quantitatively into the original 2-methyldihydroresorcinol, whereas the triketone (V) is not affected under these conditions. When heated with 5% caustic potash solution, the triketone (V) undergoes hydrolytic scission with formation of the diketo acid (VI), which then recyclizes into the corresponding derivative of 2-cyclopenten-1-one (VII):



The low rate of the C-alkylation of dihydroresorcinol derivatives and their characteristic tendency to form enol ethers are evidently to be explained by the high degree of enolization of these β-diketones, a fact that is clearly manifest when a comparative study is made of the alkylation of 3-methyltetronic acid (XI), dihydroresorcinol, dimedone (5,5-dimethyl-1,3-cyclohexanedione) [5], 2-methyl-1,3-indandione (VIII), and ketones of the cyclohexane series [5]. The sodium salt of 3-methyltetronic acid (XI) is completely enolized in aqueous solution [6], but is not methylated to an appreciable extent when boiled with methyl iodide in methanol for three hours. On the other hand, the only slightly enolized 2-methyl-1,3-indandione reacts smoothly under the same conditions with formation of 2,2-dimethyl-1,3-indandione (IX), the structure of which is confirmed by its hydrolytic scission to the known o-isobutyrylbenzoic acid (X) [7]. Unlike dihydroresorcinol, which is com-

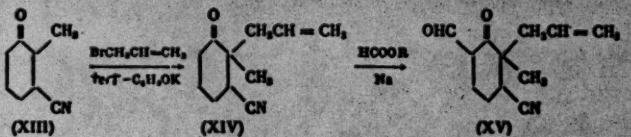
pletely enolized in aqueous solution [5], 2-methyl-1,3-indandione readily gives the C-methyl derivative (IX) even in a less polar solvent (dioxane).



(VIII) (IX) (X) (XI, XII)

(XI) R = CH_3, (XII) R = C_2H_5

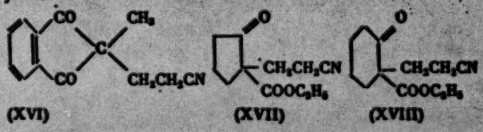
Derivatives of the feebly enolized cyclohexanone can be C-alkylated much more readily than dihydroresorcinol derivatives [9,10]. For example, when the potassium derivative of 2-methyl-3-oxocyclohexanecarbonitrile (XIII) is treated with allyl bromide in tert-butyl alcohol, rapid formation occurs of 2-allyl-2-methyl-3-oxocyclohexanecarbonitrile (XIV), the structure of which was proved by its conversion into the formyl derivative (XV) by the action of formic ester and sodium:



(XIII) (XIV) (XV)

The inhibiting effect of enolization on the C-alkylation of cyclic β-diketones can be seen from Table 1.

In order to study the effect of enolization on the ability of keto-enols to undergo Michael condensation, we investigated the cyanoethylation of the 3-alkyltetronic acids (XI) and (XII), 2-methyl-1,3-indandione, ethyl 2-oxocyclopentanecarboxylate, and ethyl 2-oxocyclohexanecarboxylate. As shown previously [1-4], heat must be applied in order to effect the reaction of 3-alkyltetronic acids, dihydroresorcinol, and dimedone with acrylonitrile in aqueous dioxane in presence of caustic soda. In contrast to these β-diketones, the only slightly enolized 2-methyl-1,3-indandione reacts fairly readily with acrylonitrile, even at 20°, and forms the 2-cyanoethyl derivative (XVI) in 55% yield.



(XVI) (XVII) (XVIII)

In aqueous solutions of dioxane in presence of one-sixth of an equivalent of caustic soda the feebly enolized ethyl 2-oxocyclopentanecarboxylate reacts vigorously with acrylonitrile at room temperature (with evolution of heat), and after only 30 minutes a 75% yield of the 2-cyanoethyl derivative (XVII) is obtained. Under the same conditions, the more strongly enolized ethyl 2-oxocyclohexanecarboxylate gives a yield of only 33% of the 2-cyanoethyl derivative (XVIII).

The deactivating effect of enolization on the cyanoethylation of carbonyl compounds under comparable conditions can be seen clearly from an examination of Tables 2 and 3.

EXPERIMENTAL

Reaction of the Potassium Derivative of 2-Methyldihydroresorcinol with Bromomethyl 1-Hydroxycyclohexyl Ketone

A solution of the potassium derivative of 2-methyldihydroresorcinol was prepared from 0.8 g of potassium

TABLE 1

Methylation of β-Dicarbonyl Compounds (Action of Methyl Iodide on the Sodium Derivatives)

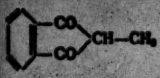
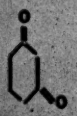
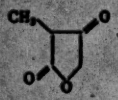
Formula of compound	Amount of enol in H_2O (%)	Solvent	Reaction temperature (°C)	Duration of reaction (hours)	Yield (%)
	0.2 [11]	Aqueous alcohol	20	2-3	75 [12]
	1.0 [11]	Methanol Dioxane	At boil 100	2 ½	67 70
	100 [3]	Methanol Dioxane Aqueous alcohol	At boil 100 20	3 ½ 3	40 [1] 0 0
	100 [6]	Methanol	At boil	3	0

TABLE 2

Cyanoethylation of β-Dicarbonyl Compounds in tert-Butyl Alcohol Solution in presence of Triton B

Formula of compound	Amount of enol in H_2O (%)	Reaction temperature (°C)	Duration of reaction (hours)	Yield [a] (%)
$CH_2(COOC_2H_5)_2$	Traces [8, 13]	30	2	83 [14]
$CH_3COCH_2COOC_2H_5$	0.5 [11]	30-40	1	50 [15]
$CH_3COCH_2COCH_3$	19 [11]	90	2	49 [15]
$C_6H_5COCH_2COCH_3$	32.4 [11]	90	2	22 [15]

and 2 g of 2-methyldihydroresorcinol (I) (m.p. 209-210°) in 15 ml of methanol, and 3 g of bromomethyl 1-hydroxycyclohexyl ketone (II) b.p. 103-105° (0.5 mm), n_D^{25} 1.5170 [16] was added. The mixture was refluxed for three hours. Methanol was distilled off under reduced pressure, and the residue was treated with 10 ml of water and 10 ml of ether. The precipitated crystals were filtered off and washed with ether. The product was 1.7 g (40%) of the enol ether (III), m.p. 135-136° (from aqueous methanol).

Found %: C 67.55; 67.48; H 8.19; 8.02

$C_{18}H_{22}O_4$. Calculated %: C 67.1; H 8.3

When the enol ether (III) was shaken in the cold with 2% hydrochloric acid, the original 2-methyldihydroresorcinol was formed in almost quantitative yield.

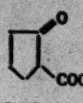
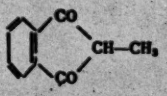
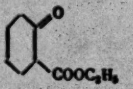
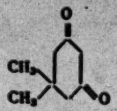
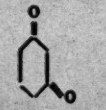
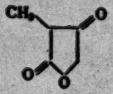
Reaction of the Potassium Derivative of 2-Methyldihydroresorcinol with 2-Bromoacetophenone

A solution of the potassium derivative of 2-methyldihydroresorcinol was prepared from 1 g of potassium and 3.2 g of 2-methyldihydroresorcinol in 25 ml of methanol, and 4.8 g of 2-bromoacetophenone was added.

[a] The yields refer to the bis-2-cyanoethyl derivatives.

TABLE 3

Cyanoethylation of ß-Dicarbonyl Compounds in Aqueous Dioxane Solution in Presence of One-Sixth of an Equivalent of Sodium Hydroxide

Formula of compound	Amount of enol in H_2O (%)	Reaction temperature (°C)	Duration of reaction (hours)	Yield (%)
	0.2 [11]	20-30	1/2	75
$CH_3COCH_2COOC_2H_5$	0.5 [11]	20 20	1/2 5	15• 50•
	1.0 [11]	20	5	55
	4.6 [11]	20	1/2	33
	95.3 [11]	100 60-70 20	3 1/2 5 5	81 [3] 56• [3] 0
	100 [8]	100 20	2 1/4 5	23•• [3] 0
	100 [8]	20	5	0

•The yields refer to bis-2-cyanoethyl derivatives.

••The reaction was carried out in presence of one equivalent of sodium hydroxide.

The mixture was refluxed for three hours. When cool, the solution was filtered and evaporated to dryness under reduced pressure. The residue was treated in the cold with sodium carbonate solution, heated for 10-15 minutes at 60-70° with methanol acidified with a few drops of concentrated hydrochloric acid (to remove traces of the enol ether), and washed with water. The product was 2.2 g (44%) of the triketone (V), m.p. 125-128° (from methanol).

	Found %:	C 73.70; 73.84; H 6.73; 6.59
$C_{23}H_{22}O_3$.	Calculated %:	C 73.75; H 6.6

Hydrolytic Scission of the Triketone (V)

A mixture of 2 g of the above-described triketone (V), 1 g of caustic potash, and 20 ml of water was

heated at 60-70° until the crystals had dissolved completely. Acidification of the cooled solution with concentrated hydrochloric acid gave a precipitate of 1.6 g (80%) of the keto acid (VII), m.p. 94-95° (from water).

Found %: C 73.73; 73.82; H 6.42; 6.66
$C_{12}H_{12}O_3$. Calculated %: C 73.7; H 6.6
Titration equivalent found: 243.6; 250
$C_{12}H_{12}O_3$. Titration equivalent calculated: 244

The 2,4-dinitrophenylhydrazone melted at 131-132° (from methanol).

Found %: N 14.57; 14.90
$C_{21}H_{20}O_7N_4$. Calculated %: N 13.20

Methylation of 2-Methyl-1,3-indandione

1. A solution of the sodium derivative of 2-methyl-1,3-indandione was prepared from 0.12 g of sodium and 0.8 g of 2-methyl-1,3-indandione (VIII) (m.p. 84-85°) in 3 ml of methanol, and 1.5 g of methyl iodide was added. The mixture was refluxed for two hours, and was then cooled and treated with a solution of 2 g of sodium carbonate. Extraction with chloroform and removal of solvent gave a residue which crystallized completely, the product being 0.8 g (87%) of 2,2-dimethyl-1,3-indandione (IX), m.p. 106-107° (from aqueous methanol). The literature gives m.p. 107-108° [17].

2. A mixture of 0.2 g of finely ground sodamide, 0.8 g of 2-methyl-1,3-indandione, and 10 ml of dioxane was stirred at 60-70° for 10 minutes and then, after the addition of 1.5 g of methyl iodide, heated for a further 20 minutes at 100°. The solution was cooled and evaporated to dryness under reduced pressure; the residue was treated with 10 ml of saturated sodium carbonate solution. The product was 0.65 g (72%) of 2,2-dimethyl-1,3-indandione (IX), m.p. 106-107° (from aqueous methanol).

When dihydroresorcinol was treated under similar conditions, practically no C-methylation occurred.

Hydrolytic Scission of 2,2-Dimethyl-1,3-indandione

A mixture of 0.6 g of 2,2-dimethyl-1,3-indandione, 0.6 g of caustic potash, and 10 ml of water was stirred at 50-60° until solution was complete (about 20 minutes). Acidification of the cooled solution with concentrated hydrochloric acid gave a precipitate of 0.6 g (86%) of o-isobutyrylbenzoic acid (X), m.p. 120-121° (from water). The literature [7] gives m.p. 120-121°.

Reaction of Allyl Bromide with the Potassium Derivative of 2-Methyl-3-oxocyclohexanecarbonitrile

A solution of potassium tert-butoxide was prepared from 0.7 g of potassium and 30 ml of tert-butyl alcohol, and 2.5 g of 2-methyl-3-oxocyclohexanecarbonitrile (XIII) (m.p. 57-58°) [18] was added. The mixture was stirred while 3 g of allyl bromide was added in portions. After a few minutes a copious precipitate of potassium bromide formed. After standing for two hours at room temperature, the solution was evaporated to dryness under reduced pressure and the residue was treated with 10 ml of water and extracted with ether. The product was 1.7 g (51%) of 2-allyl-2-methyl-3-oxocyclohexanecarbonitrile (XIV), b.p. 103-107° (2 mm); n_D^{20} 1.4850.

Found %: C 74.67; 74.52; H 8.62; 8.77; N 7.68; 7.87
$C_{11}H_{15}ON$. Calculated %: C 74.6; H 8.5; N 7.9

The semicarbazone melted at 175-176° (from aqueous methanol).

Found %: N 23.67; 23.79
$C_{12}H_{18}ON_4$. Calculated %: N 23.9

Formylation of 2-Allyl-2-methyl-3-oxocyclohexanecarbonitrile

Ethyl formate (4 g) and the above-described 2-allyl-2-methyl-3-oxocyclohexanecarbonitrile (XIV) (4.6 g) were added to 1 g of granulated sodium in 50 ml of ether. The mixture was stirred for one hour and then set aside for 12 hours at room temperature. The precipitated sodium derivative was then filtered off, washed with ether, and treated with ice and dilute (1:1) hydrochloric acid. The oil that separated was extracted with ether and vacuum-distilled. The product was 2.4 g (46%) of 2-allyl-4-formyl-2-methyl-3-oxocyclohexanecarbonitrile (XV), b.p. 123-126° (1 mm); n_D^{20} 1.5160.

	Found %:	C 70.50; 70.53;	H 7.33; 7.19;	N 6.55; 6.70
$C_{12}H_{13}O_3N$.	Calculated %:	C 70.3;	H 7.3;	N 6.8

The substance gives a dark coloration with ferric chloride, and it dissolves in cold dilute alkali.

Cyanoethylation of 2-Methyl-1,3-indandione

Acrylonitrile (4 g) was added to a solution of the sodium derivative of 2-methyl-1,3-indandione prepared from 0.08 g of caustic soda, 1.6 g of 2-methyl-1,3-indandione (VIII), and 12 ml of aqueous dioxane (1:3). The mixture was set aside at 20° for five hours and then acidified to congo red with dilute (1:1) hydrochloric acid. It was then treated with a solution of sodium carbonate, and the product was extracted with ether. When the solvent was removed, the residue crystallized completely. The product was 1.2 g (55%) of 2-methyl-1,3-dioxo-2--indanpropionitrile (XVI), m.p. 84-85° (from aqueous methanol).

	Found %:	C 72.95; 73.03;	H 5.20; 5.33;	N 6.85; 6.91
$C_{13}H_{11}O_2N$.	Calculated %:	C 73.2;	H 5.1;	N 6.6

When treated under similar conditions, dihydroresorcinol, dimedone, 2-methyldihydroresorcinol, and the 3--alkyltetronic acids (XI) and (XII) do not undergo cyanoethylation.

Cyanoethylation of Ethyl 2-Oxocyclopentanecarboxylate

To a stirred solution of 0.28 g of caustic soda in 10 ml of water, 6.4 g of ethyl 2-oxocyclopentanecarboxylate (b.p. 103-105°/15 mm; n_D^{20} 1.4505 [19]) and a solution of 4 g of acrylonitrile in 34 ml of dioxane were added in quick succession. The temperature of the solution rose slowly to 20-30°. After 30 minutes the reaction mixture was cooled with ice, acidified with dilute (1:1) hydrochloric acid to congo red, and extracted with chloroform. After removal of solvent, the residue was vacuum-fractionated. The product was 6.4 g (75%) of 1--(ethoxycarbonyl)-2-oxocyclopentanepropionitrile (XVII), b.p. 176-178° (8 mm); n_D^{20} 1.4644.

	Found %:	C 62.78; 62.95;	H 7.01; 7.11;	N 6.85; 6.93
$C_{11}H_{15}O_3N$.	Calculated %:	C 63.1;	H 7.2;	N 6.7

The semicarbazone melted at 147-148° (from aqueous methanol).

	Found %:	N 20.72; 20.85
$C_{12}H_{18}O_3N_4$.	Calculated %:	N 21.1

Cyanoethylation of Ethyl 2-Oxocyclohexanecarboxylate

When ethyl 2-oxocyclohexanecarboxylate (b.p. 103-107°/11 mm; n_D^{20} 1.4750 [19]) was cyanoethylated under the above-described conditions, no evolution of heat was observed. Treatment of 6.8 g of the 2-oxocyclohexanecarboxylic ester gave 3 g (33%) of 1-(ethoxycarbonyl)-2-oxocyclohexanepropionitrile (XVIII), b.p. 167-169° (7 mm); n_D^{20} 1.4715 [20]. In addition 2.4 g of the 2-oxocyclohexanecarboxylic ester was recovered unchanged. The semicarbazone of (XVIII) melted at 168-169° (from aqueous methanol).

	Found %:	N 19.69; 19.83
$C_{13}H_{20}O_3N_4$.	Calculated %:	N 20.0

SUMMARY

1. When the potassium derivative of 2-methyldihydroresorcinol was treated with bromomethyl 1-hydroxycyclohexyl ketone (II) in methanol solution, the corresponding enol ether (III) was formed in 40% yield. Under the same conditions, reaction between the potassium derivative of 2-methyldihydroresorcinol and 2-bromoacetophenone gave the C-derivative (V) in 44% yield.

2. When boiled for three hours with methyl iodide in a methanol medium, 3-methyltetronic acid (XI) was not methylated, whereas 2-methyl-1,3-indandione gave the C-methyl derivative (IX) in 70% yield.

3. Unlike dihydroresorcinol, 2-methyl-1,3-indandione readily undergoes C-methylation in dry dioxane.

4. In condensations with acrylonitrile, 2-methyl-1,3-indandione reacts more readily than dihydroresorcinol derivatives and 3-alkyltetronic acids.

5. In aqueous dioxane in presence of caustic alkali, the cyanoethylation of ethyl 2-oxocyclohexanecarboxylate is more difficult than that of ethyl 2-oxocyclopentanecarboxylate.

6. These examples of low nucleophilic reactivity in keto-enol compounds is to be explained by the deactivating effect of enolization.

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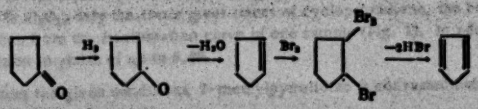
POSSIBILITY OF FORMING CYCLOPENTADIENE FROM HETEROCYCLIC COMPOUNDS CONTAINING FIVE CARBON ATOMS

N.I. Shuikin and V.A. Tulupov

Cyclopentadiene was synthesized by Zelinsky and Levina [1] in accordance with the scheme:



As is well known, cyclopentadiene is formed in the high-temperature treatment of coal, petroleum, hydrocarbon gases, and other organic substances. For example, it has been isolated from the products obtained in the coking of coal [2] and in the cracking of gas oil [3, 4]. Volzhinsky and Shcheglova [5] found that a fraction of boiling range 28-50° obtained in the cracking of kerosene at low pressure contained about 35% of dienes, mainly cyclopentadiene. There are references to the presence of cyclopentadiene in pyrolysis products from natural gas [6], and also in illuminating gas and water gas [7]. Kazansky and Plate [8] detected cyclopentadiene in pyrolysis products from cyclopentane. In addition to the latter, cyclopentadiene is formed also as the result of a disproportionation reaction between hydrogen and cyclopentene, which occurs at 450° and 500° on an alumina-chromia catalyst and at 180-200° on palladium black [9]. Cyclopentadiene is formed also in the pyrolysis of the lower-paraffins [10], in the pyrolysis of olefins [11], and even in the cracking of phenol and alkylbenzenes [12].

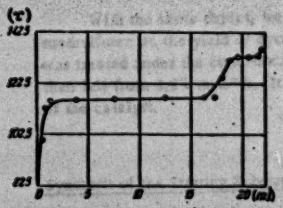


Fig. 1. Fractionation curve for the transformation products of piperidine

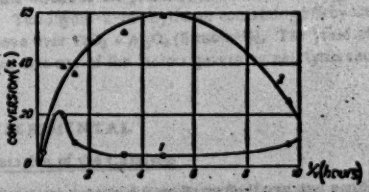


Fig. 2. Dependence of the yields of cyclopentadiene (Curve 1) and piperylene (Curve 2) on the reciprocal of the space velocity for the passage of tetrahydro-2-methylfuran over $TiO_2 + Al_2O_3$ (5 mole-%)

The problem of the direct preparation of cyclopentadiene by the catalytic cyclization of piperylene was first tackled by Kennedy and Hetzel [13], who showed that a condensate containing up to 9% of cyclopentadiene is obtained from piperylene at 600-620° under low pressure. On the other hand, various investigations [14-17] have shown that certain heterocyclic compounds may be converted into piperylene. It was considered to be of interest, therefore, to determine whether it is possible in principle to prepare cyclopentadiene directly from simple heterocyclic compounds under the conditions required for the cyclization of piperylene. With this object

we investigated the contact-catalysis reactions of tetrahydro-2-methylfuran, tetrahydro-2 methylthiophene, 2--methylpyrrolidine, and piperidine.

The most accessible of these compounds is tetrahydro-2-methylfuran, and most of the experiments designed to determine the optimum conditions for reaction, to elucidate various matters relating to the mechanism of the formation of cyclopentadiene, and to select the most active catalyst were therefore carried out with this substance. It was shown that the optimum conditions of temperature and pressure are 600° and 30-35 mm. Of the catalysts investigated - Al_2O_3, Al_2O_3 + MnO (1:2), $ZrSiO_4$, TiO_2 + Al_2O_3 (5, 10, and 25 mole-% of Al_2O_3), and TiO_2 + ThO_2 (3:1) - the mixed catalyst TiO_2 + Al_2O_3 (5 or 10% Al_2O_3) was found to be the most active. Hence, in giving the results of our investigation into the reactions of the above-mentioned heterocycles, we shall confine ourselves to the work with titania-alumina catalysts.

We found that, over the catalyst TiO_2 + Al_2O_3 (5 mole-% Al_2O_3) at 600° and 30-35 mm pressure, tetrahydro-2-methylfuran and tetrahydro-2-methylthiophene, passed at a space velocity of 1 $hour^{-1}$, are converted into cyclopentadiene at a yield of about 20%. When passed over TiO_2 + Al_2O_3 (10 mole-%) at a space velocity of 0.2 $hour^{-1}$, they give a yield of only about 5% of cyclopentadiene. In both cases an appreciable amount of piperylene is also formed (see below). As regards 2-methylpyrrolidine and piperidine, in contact with TiO_2 + Al_2O_3 (5 mole-% Al_2O_3) only the latter gives traces of cyclopentadiene, the bulk of the catalyzate being pyridine, as can be seen from the fractionation curve of one sample (Fig. 1). In addition to pyridine, pyrrole is obtained in this reaction in yields of up to 5.4%.

Under the given conditions, 2-methylpyrrolidine is converted mainly into 2-methylpyrrole.

In order to elucidate certain matters relating to the mechanism of the formation of cyclopentadiene, we investigated the dependence of the yields of cyclopentadiene and piperylene on the time of contact of tetrahydro-2-methylfuran with the catalyst. In addition, a comparison was made of the degrees of conversion of piperylene and of tetrahydro-2-methylfuran into cyclopentadiene for identical times of contact. It was found that for a given catalyst tetrahydro-2-methylfuran gave a higher yield of cyclopentadiene than piperylene did, although the reverse would have been expected if the formation of cyclopentadiene proceeds through the intermediate stage of piperylene. It was shown also that, in the transformation of tetrahydro-2-methylfuran, the formation of cyclopentadiene and the formation of piperylene (Fig. 2) proceed both as parallel and as successive reactions, the yield maxima being displaced with respect to each other. For a certain time of contact (Fig. 2) the two reactions appear to be independent, but after a sufficiently long period of contact cyclopentadiene is formed not only directly from tetrahydro-2-methylfuran, but also indirectly via piperylene.

With the same object, we investigated the effect of the presence of bases in the original tetrahydro-2-methylfuran on the yield of cyclopentadiene. Tetrahydro-2-methylfuran containing 5% by weight of piperidine was treated under the conditions indicated above over TiO_2 + Al_2O_3 (5 mole-%). The yield of cyclopentadiene then fell from 8.2% to 0.7%. It was thus shown that one of the factors governing catalytic action was the "acidity" of the catalyst.

EXPERIMENTAL

Synthesis of the Starting Substances and Preparation of the Catalysts

Tetrahydro-2-methylfuran and piperidine were prepared from 2-methylfuran and pyridine respectively by hydrogenation (at 125° and 150° respectively) by the flow method in presence of nickel deposited on a nickel-aluminum alloy (27% Ni) prepared by a method previously described by one of us [18]. The hydrogenation products were fractionated over sodium through a 30-plate column. The properties of the products were: tetrahydro-2-methylfuran - b.p. 79-79.2° (745 mm); d_4^{20} 0.8582; n_D^{20} 1.4087; piperidine - b.p. 105.5° (760); d_4^{20} 0.8640; n_D^{20} 1.4592. According to the literature, tetrahydro-2-methylfuran [19] has b.p. 78.5-80° (746); d_4^{20} 0.8582; n_D^{20} 1.4072; and piperidine [20] has b.p. 106°; d_4^{20} 0.8612; and n_D^{20} 1.4523.

Tetrahydro-2-methylthiophene and 2-methylpyrrolidine were prepared by reaction of tetrahydro-2-methylfuran with hydrogen sulfide and ammonia respectively in presence of catalysts [20]. Each catalyzate was fractionated twice from a Favorsky flask, and tetrahydro-2-methylthiophene and 2-methylpyrrolidine were prepared in yields of 36% and 20% respectively. The constants of the products were: tetrahydro-2-methylthiophene - b.p. 131-132° (757 mm); d_4^{20} 0.9533; n_D^{20} 1.4907; and 2-methylpyrrolidine - b.p. 104-105° (750 mm); d_4^{20} 0.8312; n_D^{20} 1.4380. Yuryev gives the following constants [20]: tetrahydro-2-methylthiophene - b.p. 131.2-131.5°; d_4^{20}

0.9541; n_D^{20} 1.4922; 2-methylpyrrolidine - b.p. 104-104.5° (755 mm); d_4^{20} 0.8307; n_D^{20} 1.4372.

Piperylene was obtained by fractionation of the commercial product through a 70-plate column. A narrow fraction was collected; boiling range 41.7-43.8° (757 mm); d_4^{20} 0.6834; n_D^{20} 1.4317; it was a mixture of cis- and trans-piperylenes. For a mixture of cis- and trans-piperylenes, the literature [21] gives b.p. 43°; d_4^{20} 0.685; n_D^{20} 1.4309.

Samples of titania-alumina catalyst having alumina contents of 5 and 10 mole-% were prepared by carefully grinding a mixture of pure titania and freshly precipitated aluminum hydroxide in a mortar. The mixture was formed into the form of small balls, and these were given a preliminary drying at 150°.

Catalytic Transformations of Tetrahydro-2-methylfuran, Tetrahydro-2-methylthiophene, 2-Methylpyrrolidine, and Piperidine

The experiments were carried out at 600° and 30-40 mm pressure in a silica tube of internal diameter 16 mm. The substances were passed to the catalysis tube from an automatic buret. In the experiments on tetrahydro-2-methylfuran, piperylene, and piperidine, we took 50 g of each substance, and in those on tetrahydro-2-methylthiophene and 2-methylpyrrolidine we took 25 g and 20 g respectively. In the kinetic experiments 15 g of tetrahydro-2-methylfuran was taken. The catalysis products were collected in a water-cooled receiver and in three successive traps, of which two were immersed in a mixture of dry ice and methanol, and the third was immersed in liquid nitrogen. The extent of cracking was determined by the weight of liquid catalyzate. Analysis for the cyclopentadiene content of the catalyzate was carried out by the method propored by Afanasyev [22]. The total diene content was determined by reaction with maleic anhydride in accordance with Krauze, Kogan, and Polievktova's method [23], the piperylene content being found by difference. The catalyzates obtained in experiments with tetrahydro-2-methylfuran and piperidine were fractionated through a column, but the tetrahydro-2-methylthiophene and 2-methylpyrrolidine catalyzates were fractionated from a Favorsky flask. The results obtained in experiments on tetrahydro-2-methylfuran and tetrahydro-2-methylthiophene are given in Table 1.

TABLE 1

Transformations of Tetrahydro-2-methylfuran and Tetrahydro-2-methylthiophene in presence of $TiO_2 + Al_2O_3$ at 600°

Expt. No.	Starting substance	Content in catalyzate (mole-%)	Experimental conditions: Pressure (mm)	Experimental conditions: Space velocity ($hour^{-1}$)	Yield of catalyzate (% by wt.)	Yield of dienes (%): Cyclopentadiene	Yield of dienes (%): Piperylene
1	Tetrahydro-2-methylfuran	5	30-35	1	95.0	18.7	40.0
2	Tetrahydro-2-methylfuran	5	30-35	0.5	93.7	6.2	48.3
3	Tetrahydro-2-methylfuran	10	30-40	0.2	70.0	4.6	28.5
4	Tetrahydro-2-methylfuran + 5% piperidine	5	30-40	0.5	89.2	0.7	33.4
6	Tetrahydro-2-methylthiophene	5	30-35	1	95.4	20.3	42.1
7	Tetrahydro-2-methylthiophene	10	30-35	0.2	68.7	5.0	27.9

The catalyzates of Experiments 1, 2, and 3 were combined and fractionated through a 30-plate column. The following fractions were collected at 751 mm: Fraction I, b.p. 24-41° (5.7 g); d_4^{20} 0.6375; n_D^{20} 1.3824; bromine value 203.1; content of unsaturateds 89.9% calculated as C_5; Fraction II, b.p. 41-44° (83.7 g); d_4^{20} 0.6824; n_D^{20} 1.4329; Residue (12.3 g), which was not investigated. The catalyzates of Experiments 6 and 7 were distilled at 757 mm from a Favorsky flask. Two fractions were collected: Fraction of b.p. 25-41° (1.7 g); n_D^{20} 1.3850 and Fraction of b.p. 41-44° (23.4 g); n_D^{20} 1.4330; they were not investigated further. The results of the kinetic measurements on tetrahydro-2-methylfuran are given in Tables 2 and 3.

TABLE 2

Yield of Cyclopentadiene in the Transformations of Tetrahydro-2-methylfuran and Piperylene over $TiO_2 + Al_2O_3$

Expt. No.	Content of Al_2O_3 in catalyzate (mole-%)	Experimental conditions: Pressure (mm)	Temperature (°C)	Space velocity ($hour^{-1}$)	Starting substance	Yield of cyclopentadiene (% of theory)
1	5	30-35	600	0.5	Tetrahydro-2-methylfuran	6.2
2	5	30-35	600	0.5	Piperylene	2.0
3	10	30-40	600	0.2	Tetrahydro-2-methyl furan	4.6
4	10	30-40	600	0.2	Piperylene	2.9

TABLE 3

Dependence of the Yields of Cyclopentadiene and Piperylene on the Space Velocity of the Passage of Tetrahydro-2-methylfuran over $TiO_2 + Al_2O_3$ (5 mole-%) at 600° and 25-30 mm

Expt. No.	Space velocity ($hour^{-1}$)	Yield of dienes (%): Cyclopentadiene	Piperylene	Expt. No.	Space velocity ($hour^{-1}$)	Yield of dienes (%): Cyclopentadiene	Piperylene
1	5	5.1	Not investigated	4	0.3	4.6	52.3
2	1	20.0	39.7	5	0.2	3.6	59.3
3	0.7	9.4	36.3	6	0.1	6.5	25.1

The transformations of pipendine (50 g) were investigated in presence of $TiO_2 + Al_2O_3$ (5 mole-% Al_2O_3). In the catalyzate, which amounted to 33.5 g, only traces of cyclopentadiene could be detected. The catalyzate was fractionated through a 30-plate column (see Fig. 1), and the following fractions were collected:

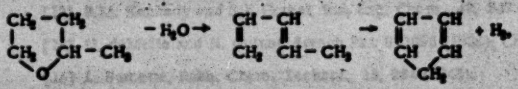
	B.p. (°C)	Amount (g)	Yield (% of catalyzate)	d_4^{20}	n_D^{20}
Fraction I	82-116	0.8	2.3	—	1.4420
Fraction II	116	23.0	68.7	0.9779	1.5073
Fraction III	116-130	1.7	5.1	0.9738	1.5062
Fraction IV	130-132	1.8	5.4	0.9697	1.5044
	Residue	5.2	15.5	—	—

The individual compounds obtained were pyridine (Fraction II) and pyrrole (Fraction IV). For pyrrole the literature [24] gives b.p. 130-131°; d_4^{20} 0.9891; and n_D^{20} 1.5035.

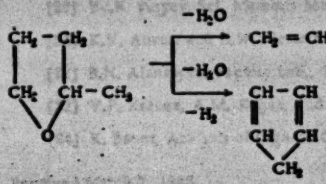
The transformations of 2-methylpyrrolidine were also carried out in presence of $TiO_2 + Al_2O_3$ (5 mole-% Al_2O_3), the temperature being 600° and the space velocity 0.5 $hour^{-1}$. From 20 g of 2-methylpyrrolidine 19.0 g of catalyzate was obtained, and this was fractionated from a flask fitted with a column. A very small amount (0.5 g) came over in the range 79-143° (741 mm), and the bulk (14.7 g) came over at 148-151°. This substance gave a reaction for pyrrole and had d_4^{20} 0.9289 and n_D^{20} 1.5003. For 2-methylpyrrole Yuryev gives the following constants [20]: b.p. 148.5-150°; d_4^{20} 0.9295 and n_D^{20} 1.5012. The small residue was not investigated. In the course of the transformations of the nitrogen-containing heterocycles, a very small amount of ammonia was formed.

On analogy with certain other reactions peculiar to heterocycles, it might be expected that all of the heterocycles studied would be converted into cyclopentadiene. Our investigation, however, indicates that there is an essential difference between the oxygen- and sulfur-containing hydrogenated heterocycles on the one hand and the nitrogen-containing hydrogenated heterocycles on the other. In the given case the reaction of cyclopentadiene formation over a titania-alumina catalyst is of limited scope.

Owing to the absence of sufficient experimental material, it is not yet possible to state the true significance of the important fact that we have noted. However, on the basis of our results we may make an attempt to elucidate the mechanism of the formation of cyclopentadiene. There is no discussion of this matter in the literature, and the scheme that is generally applicable to the dehydration of ethers does not cover all of the products obtained in the reaction under consideration. In fact, if we were concerned with successive dehydration and dehydrocyclization reactions so that tetrahydro-2-methylfuran would first give piperylene, which would then undergo dehydrocyclization into cyclopentadiene:



then the yield of cyclopentadiene obtained by passage of piperylene over the same catalyst should be greater than that obtained from tetrahydro-2-methylfuran. The behavior observed, however, is the reverse. Moreover, kinetic measurements show that cyclopentadiene and piperylene are formed as the result of reactions that occur in parallel. Hence, the reaction being catalytic, it would appear that adsorption of tetrahydro-2-methylfuran on the catalyst surface forms a complex that reacts with formation of both compounds:



Experiment indicates that the nature of the catalyst is an important factor in the process, the extent of conversion being determined, therefore, by an energy factor.

SUMMARY

1. An investigation was made into the possibility of the formation of cyclopentadiene from tetrahydro-2-methylfuran, tetrahydro-2-methylthiophene, 2-methylpyrrolidine, and piperidine in presence of a titania-alumina catalyst at 600° at low pressure.

2. It was shown that, under these conditions, only tetrahydro-2-methylfuran and tetrahydro-2-methylthiophene give cyclopentadiene, the yield being about 20%.

3. The main reaction undergone by piperidine and 2-methylpyrrolidine was dehydrogenation into pyridine and 2-methylpyrrole respectively. In addition, piperidine gave 5% of pyrrole.

4. It was shown that the formation of cyclopentadiene from tetrahydro-2-methylfuran over a titania-alumina catalyst occurs as a result of both parallel and successive reactions.

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CONTACT-CATALYSIS REFINING OF TUIMAZIN GASOLINE

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As is well known, straight-run Tuimazin gasoline – owing to its low quality, which results from the high content of n-alkanes and organically bound sulfur – cannot be used in automobile engines without being refined. In the present investigation we studied the possibility of improving the performance properties of Tuimazin straight-run gasoline by desulfurization and modification of composition in a two-stage contact-catalysis process.

In the first stage of the refining the catalyst used was aluminum chloride, which is known to effect simultaneously the desulfurization of the gasoline and the isomerization of the n-alkanes present into branched forms. In the second stage the desulfurized gasoline was submitted to Zelinsky dehydrogenational catalysis. In this process the cyclohexane hydrocarbons, both those present in the original gasoline and those formed by the isomerization of cyclopentane hydrocarbons, were converted into the corresponding aromatic hydrocarbons.

There are various references in the literature [1-4] to the ability of aluminum chloride to give complexes with various organic sulfur compounds, both aliphatic and aromatic. Other authors [5] have noted that the response of gasolines to TEL (tetraethyllead) additions is much greater after treatment with aluminum chloride. Zelinsky and Yuryev [6] showed that with the aid of aluminum chloride it is possible to effect almost complete desulfurization of gasoline containing 0.392% of organically bound sulfur. Similar results were obtained by Goldshtein and Semenova [7] for the aluminum chloride desulfurization of gasoline containing thiols, aliphatic sulfides, and thiophene. The occurrence of the isomerization of mono- and di-alkylcyclopentanes into cyclohexane hydrocarbons in presence of aluminum chloride was demonstrated by Nenitzescu and Cantuniari [8] and others [9]. This reaction was studied in detail by Turova-Polyak and coworkers [10]. As regards the isomerization of n-alkanes in presence of aluminum chloride, several review articles have appeared [11-13].

In determining the conditions for the refining of Tuimazin gasoline, we used aluminum chloride with the object of removing organically bound sulfur from the gasoline, converting five-membered cycloalkanes into six-membered cycloalkanes (which were subsequently dehydrogenated into aromatic hydrocarbons), and isomerizing n-alkanes into branched forms. The results of the investigation showed that the two-stage refining (reforming) of Tuimazin gasoline (boiling limit 200°, octane rating 37.5 without TEL and 59.6 with 1.5 ml of TEL) was able to raise the octane rating to 50 without TEL and to 71.6 with 1.5 ml of TEL. This improvement in the performance properties of the gasoline is to be attributed to complete desulfurization, aromatization of cycloalkanes, and isomerization of n-alkanes.

EXPERIMENTAL

The following samples of Tuimazin gasoline were submitted to the refining process: 1) the whole gasoline, boiling range 34-200°; 2) the gasoline after removal of the head fraction, boiling range 60-200°; and 3) the gasoline after removal of the heptane-methylcyclohexane fraction (91-103°). Removal of the head fraction was carried out with the object of avoiding its loss during the aluminum chloride treatment. Removal of the heptane-methylcyclohexane fraction had the object of determining the possibility of obtaining toluene by its catalytic dehydrogenation at 300°. The properties of the original samples of Tuimazin gasoline are given in Table 1.

The separation of the head and heptane-methylcyclohexane fractions was carried out with the aid of a 19-plate column. The head fraction, amounting to 10% of the gasoline, was purified from sulfur compounds by means of sulfuric acid (3% on the weight of the fraction) and was subsequently mixed with the refined part of the gasoline.

TABLE 1

Properties of the Original Samples of Tuimazin Gasoline

Sample No.	Gasoline	Boiling range (°C)	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by wt)	Sulfur content (% by wt)	Octane rating by the motor method		
							without TEL	with 1 ml TEL	with 1.5 ml TEL
1	Whole gasoline	34-200	1.4103	0.7305	8.0	0.08	37.5	52.6	59.6
2	Gasoline without head fraction	60-200	1.4149	0.7418	8.0	0.08	–	–	–
3	Gasoline without 91-103° fraction	34-200	1.4122	0.7332	7.5	0.079	39.0	–	60

TABLE 2.

Characteristics of Samples of Refined Tuimazin Gasoline

Sample No.	Sample of refined gasoline	Yield after $AlCl_3$ treatment (% by wt)	Boiling range (°C)	n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by wt)	Octane rating by the motor method		
							without TEL	with 1 ml TEL	with 1.5 ml TEL
1	Whole gasoline after catalysis	–	47-200	1.4195	0.7460	22.0	40.0	62.0	–
2	Whole gasoline after treatment with $AlCl_3$ (6%) at 80° for 6 hrs.	97.8	40-200	1.4128	0.7335	8.5	40.5	60.0	64.0
3	Sample No. 2 after catalysis	–	48-200	1.4270	0.7579	28.0	44.0	64.0	67.0
4	Gasoline without 91-103° fraction after treatment with $AlCl_3$ under the same conditions	97.0	40-200	1.4127	0.7346	8.0	40.0	59.3	63.4
5	Sample No. 4 after catalysis	–	47-200	1.4232	0.7523	22.0	48.0	65.0	68.0
6	Gasoline without head fraction after treatment with $AlCl_3$ (10%) at 80° for 20 hours	96.3	60-200	1.4114	0.7392	8.0	–	–	–
7	Sample No. 6 after catalysis and admixture with the head fraction	–	42-200	1.4238	0.7491	25.0	50.0	–	71.6

Experimental Conditions and Procedure

The following factors were varied in the experiments on the treatment of gasoline with aluminum chloride: the amount of aluminum chloride was varied from 6% to 10%, the duration of reaction from 6 hours to 20 hours, and the temperature from 80° to 100°. In each experiment 500 g of the gasoline was taken. The experiments were carried out in a three-necked flask fitted with mechanical stirrer, reflux condenser, and ther-

mometer. The condenser was connected to a trap cooled with dry ice, and this was followed by a wash bottle containing plumbite solution. After the catalysis operation, the gasoline was separated from aluminum chloride, washed - first with water, then with 10% caustic soda, and finally with water - and then dried with calcium chloride. The loss of gasoline in this treatment was 3.5-4%.

The catalyzates were characterized by refractive index, density, boiling range, and content of aromatic hydrocarbons (sulfuric acid method). The content of sulfur compounds was determined by the lamp method (All-Union State Standard 17872-39), and octane ratings were determined with a Vokesh engine. The dehydrogenation of the gasoline was carried out in a flow apparatus of the usual type at 300-305° (when platinized charcoal was used) and at 310-315° (when Ni on Al_2O_3 + SiO_2 was used).

TABLE 3

Group Compositions of the Original and Refined Tuimazin Gasolines (by Aniline Point Method)

Hydrocarbon content (% by weight)	Original whole gasoline	Gasoline after $AlCl_3$ treatment	Hydrocarbon content (% by weight)	Original whole gasoline	Gasoline after $AlCl_3$ treatment
Aromatics	9.0	8.5	Cyclohexanes	13.5	22.4
Cyclopentanes	9.5	0.6	Paraffins	68.0	68.5

TABLE 4

Characteristics of the Heptane and Octane Isomerizates

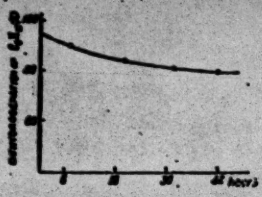
Expt. No.	Original hydrocarbon	Experimental conditions: Amount of $AlCl_3$ (% by weight)	Time of contact (hours)	Yield of isomerizate (% by wt. on original hydrocarbon)	Properties of isomerizates* Boiling range (°C)	n_D^{20}	d_4^{20}	Content of isoparaffins (% by wt. on original hydrocarbon)
1	Heptane	6	6	87.0	38-112	1.3855	0.6799	10.5
2	Ditto	8	6	86.0	40-112	1.3835	0.6751	11.2
3	"	6	8	88.0	40-112	1.3852	0.6753	12.0
4	"	6	12	85.0	41-112	1.3850	0.6755	12.5
5	Octane	6	8	90.5	43-146	1.3941	0.6965	11.0
6	Ditto	6	8	90.0	43-150	1.3948	0.6968	11.5

*In order to establish the structure of the heptane isomers we separated the 80-90° fraction from the combined isomerizate. Raman spectra measurements by M.I. Batuev showed that this fraction consisted mainly of 2,4-dimethylpentane, very small amounts of 2,2-dimethylpentane and 2,2,3-trimethylbutane also being present.

Catalysts. The catalysts used, (platinized charcoal containing 10% of platinum, and nickel on a silica-alumina mixture, 30% Ni) were prepared by the procedure developed by Shuikin and coworkers. The volume of reduced catalyst was 150 ml. The space velocity for the passage of the gasoline was taken to be 0.4 $hour^{-1}$. The variation in the activity of platinized charcoal during the dehydrogenation of gasoline is shown in the figure. In this reaction, the nickel catalyst differed from the platinized charcoal in having a somewhat lower stability, but it could be regenerated about nine times. After regeneration with air at 300° for 4-5 hours and reduction with hydrogen at 350°, the catalyst again acquired high activity (the extent of the dehydrogenation of cyclohexane was 95-90%). The extent of the isomerization of five-membered cycloalkanes into six-membered cycloalkanes was established by dehydrogenation of gasoline after the first stage of refining, a platinized charcoal catalyst (10% Pt) being used.

In the catalytic treatment the content of aromatics in this gasoline was raised from 8% to 28%. The increase in the content of aromatics attributable to isomerization of cyclopentanes into cyclohexanes was 6% (see

samples No. 1 and No. 3 in Table 2). The optimum conditions for this isomerization were found to be: duration of catalytic treatment 6 hours, amount of aluminum chloride 6% on weight of original gasoline, temperature 80°. Raising of the temperature to 100° in the treatment of gasoline in presence of aluminum chloride does not improve the quality of the treated gasoline.



Variation in the activity of platinized charcoal with time in the aromatization of Tuimazin gasoline. Control experiments with cyclohexane.

With increase in the time of contact and in the amount of aluminum chloride, there was an increase in the isoparaffin content of the gasoline and therefore in its octane rating, which was raised to 71.6 (see Table 2, sample No. 7), i.e. 12 points higher than that of the original gasoline. The properties of the samples of refined gasoline are given in Table 2.

It may be concluded from the results presented in Table 2 that the use of the two-stage process enables a high level of refining to be attained in the treatment of Tuimazin gasoline, this being the result of the aromatization of cycloalkanes, the partial isomerization of n-alkanes, complete desulfurization (which results in a higher response of the gasoline to additions of TEL), and the removal of cyclopentane hydrocarbons, which, beginning with ethylcyclopentane, have low octane ratings. It should be noted that one single portion of aluminum chloride can be used effectively in three operations. Experiment shows that the octane rating of the gasoline can be raised to 64 (with 1.5 ml of TEL), i.e. by 4.4 points, in the first stage of the refining. The change in the chemical group composition in the first stage of the refining is shown in Table 3.

Table 3 shows that, as a result of the isomerization of the cyclopentane hydrocarbons, the content of cyclohexane hydrocarbons in the gasoline may be increased by 8.9%.

The occurrence of the isomerization of the n-alkanes of the gasoline was confirmed in separate experiments on pure heptane and octane.

Isomerization of n-Alkanes in Presence of Aluminum Chloride

Isomerization experiments were carried out on pure heptane and octane, which were first distilled through a 28-plate column. They had the following constants, which were close to values reported in the literature [14]: heptane - b.p. 98.6° (corrected), n_D^{20} 1.3875; d_4^{20} 0.6843; octane - b.p. 126.0° (corrected), n_D^{20} 1.3970; and d_4^{20} 0.7020. The catalytic reaction was carried out at 100° at atmospheric pressure for 6-12 hours. The treatment of the heptane and octane isomerizates was similar to that described above. The contents of isoparaffins were determined by a method described by Moldavsky and Livshits [15]. The evolved gas was analyzed in an Orsat-Lunge apparatus; it consisted entirely of saturated hydrocarbons. The experimental conditions and the properties of the isomerizates are given in Table 4.

The data presented in Table 4 show that, with increase in the amount of aluminum chloride and in the time of contact, there is an increase also in the isoparaffin content of the isomerizate. A partial cracking of the hydrocarbons is also to be observed. When the "whole" gasoline was treated with aluminum chloride under our conditions, cracking occurred to such a small extent that the boiling range of the gasoline remained practically unchanged. Losses in the form of gas did not generally exceed 3.5-4%. The possibility cannot be excluded that the absence of cracking is to be explained by the suppression of the aggressive action of aluminum chloride that has not entered into complex formation by the complexes formed by part of the aluminum chloride with sulfur compounds [1] and aromatic compounds [16].

SUMMARY

1. It was shown that Tuimazin gasoline can be completely desulfurized by treatment with aluminum chloride (6-10%). When the fact that one portion of aluminum chloride can be used for three successive operations is taken into account, it is found that its consumption does not exceed 2-3.5% on the weight of gasoline.

2. It was established that the desulfurization was accompanied by simultaneous isomerization of cyclo-

pentanes into cyclohexanes (the content of cyclohexane hydrocarbons was increased by 8.9%) and of n-alkanes into isoparaffins (to the extent of 10-12%).

3. As the result of a two-stage refining process, the octane rating of the gasoline was raised to 71.6 (with 1.5 ml of TEL), i.e. 10 points higher than that of the original gasoline.

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POLYMERIZATION AND COPOLYMERIZATION OF N-VINYL COMPOUNDS

COMMUNICATION 2. SOME CHARACTERISTICS OF THE COPOLYMERIZATION OF VINYL ACETATE WITH 9-VINYLCARBAZOLE AND THE PROPERTIES OF THE COPOLYMERS

S.N. Ushakov and A.F. Nikolaev

We have shown in a previous communication that the addition of 9-vinylcarbazole to vinyl esters greatly reduces the rate at which they polymerize [1]. Values found for the copolymerization constants r_1 and r_2 for vinylcarbazole and vinyl esters (the formic, acetic, propionic, and butyric esters) indicate that the activities of vinylcarbazole and the vinyl ester in the copolymerization reaction are greatly different. Vinylcarbazole is always the more active component. As knowledge of the copolymerization constants does not allow us to obtain a complete picture of the behavior of the mixture of monomers in the copolymerization reaction or to predict certain properties of the copolymer, we have now made a more detailed study of the system vinyl acetate–vinylcarbazole. In studying this system we also had the object of verifying our hypothesis concerning the dependence of the molecular weight of the copolymers on the rate of the copolymerization reaction in such systems. The procedure used for the copolymerization reaction and for the isolation and purification of the copolymers was described in the previous communication.

Effect of Temperature. The effect of temperature on the rate of copolymerization of vinyl acetate and vinylcarbazole was studied at 65°, 80°, and 100°. At each temperature 10-12 different ratios of components were examined. It will be seen from Fig. 1 that the rate of copolymerization rises with rise in reaction temperature for all component ratios. Whereas at 80° and 100° copolymerization was observed at all monomer ratios, at 65° it occurred only at certain ratios; when the mole percentage of vinylcarbazole in the original mixture was in the range 10-35, no copolymer formation was observed in the course of nine hours in presence of 0.5% of benzoyl peroxide. This result, which was observed for the first time, suggests a more critical attitude to certain statements concerning the absence of copolymerization for various monomer pairs [2, 3]. When copolymerization trials are being carried out, it is necessary to take the initial composition of the mixture, the temperature, the duration of the process, and the initiator concentration into account. When due account is taken of these factors and reaction conditions are suitably chosen, there can be no doubt that copolymers will be obtained from compounds previously considered to be incapable of forming copolymers.

Effect of the Initial Composition of the Mixture on the Composition of the Copolymer. The effect of the composition of the monomer mixture on the composition of the copolymer formed was studied for twelve different mixtures. All of the experiments were carried out at 100° in presence of 0.5% of benzoyl peroxide. The results are given in Table 1.

It will be seen from Table 1 that all of the copolymers are enriched in vinylcarbazole with respect to the initial mixture, but the extent of the enrichment falls as the vinylcarbazole content of the initial mixture increases.

Effect of the Benzoyl Peroxide Concentration. The effect of the concentration of benzoyl peroxide on the rate of copolymerization of vinyl acetate and vinylcarbazole was studied for three different monomer mixtures. All of the experiments were carried out for one hour at 100°. The benzoyl peroxide concentration was varied from zero to 2%. The results are given in Table 2, and it will be seen from this table and from Fig. 2 that with rise in the concentration of benzoyl peroxide the rate of copolymerization rises, the mean rate being proportional to the square root of the initial benzoyl peroxide concentration (the mean rate of the process is expressed as percentage conversion per hour).

In experiments carried out at a molar ratio of vinyl acetate to vinylcarbazole of 10:1 in absence of benzoyl

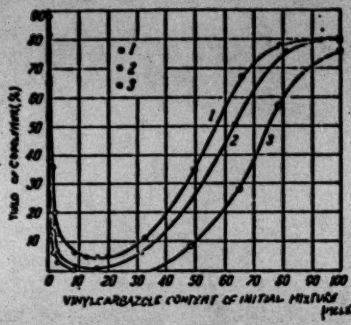

Fig 1. Dependence of the rate of copolymerization of vinyl acetate and vinylcarbazole on the reaction temperature: 1 - 100°; 2 - 80°; 3 - 65°.

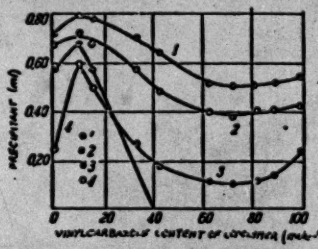

Fig. 3. Dependence of the solubility of vinyl acetate-vinylcarbazole copolymers on their vinylcarbazole contents: 1 - solubility in dioxane; 2 - solubility in chloroform; 3 - solubility in acetone; 4 - solubility in benzene.

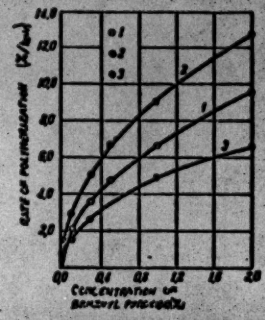

Fig. 2. Effect of the benzoyl peroxide concentration on the rate of copolymerization of vinyl acetate and vinylcarbazole: 1) molar ratio of vinyl acetate to vinylcarbazole 10 : 1; 2) 2 : 1; 3) 1 : 1.

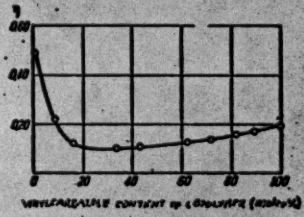

Fig. 4. Dependence of the intrinsic viscosities of the copolymers on their composition.

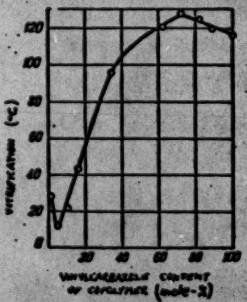

Fig. 5. Dependence of vitrification temperature on composition for vinyl acetate-vinylcarbazole copolymers.

peroxide, no copolymer formation was observed in the first hour, whereas in systems of high vinylcarbazole content (molar ratios of 2 : 1 and 1 : 1) some copolymer had already formed within the first hour. The amount formed increased with increase in the vinylcarbazole content of the initial mixture.

Solubility. The solubilities of vinyl acetate-vinylcarbazole copolymers of various compositions were determined in thirteen solvents. Solubility was determined qualitatively as follows: 10 ml of solvent was poured over 10 mg of the substance in a test tube, and the system was kept for 24 hours at 20°; the copolymer was considered to be soluble when a homogenous solution was obtained. It was found that all of the copolymers were soluble in dioxane, chloroform, and benzene, but insoluble in petroleum ether. Copolymers having low contents of vinylcarbazole (up to 30 mole-%) were soluble also in acetone, ether, carbon tetrachloride, and

TABLE 1

Effect of the Composition of the Initial Mixture on the Composition of the Copolymer

Molar ratio of vinyl acetate to vinyl carbazole	Yield of copolymer (%)	Nitrogen content of copolymer (%)	Vinylcarbazole content (mole-%)		
			in initial mixture M_2^0	in copolymer M_2^1	$\frac{M_2^1}{M_2^0}$
VA	64.65	—	—	—	—
100.22	37.06	0.40	0.99	2.58	2.61
50.00	20.12	1.41	1.97	9.72	4.95
30.25	11.87	2.10	3.21	15.38	4.78
20.14	9.12	2.73	4.73	21.20	4.48
10.10	6.68	3.85	9.01	33.57	3.73
8.05	4.98	4.17	11.37	37.61	3.31
5.04	5.09	4.68	16.56	44.85	2.80
3.01	7.07	5.40	24.89	56.54	2.30
2.03	10.67	5.80	33.01	64.00	1.94
1.00	35.34	6.24	50.50	73.40	1.45
0.51	67.48	6.61	66.30	81.82	1.23
0.25	78.02	6.98	79.00	89.24	1.13
VC	79.90	7.24	100.00	100.00	1.00

TABLE 2

Effect of the Benzoyl Peroxide Concentration on the Rate of Copolymerization of Vinyl Acetate (M_1^0) and Vinylcarbazole (M_2^0)

Amount of monomer ($\times 10^{-2}$ mole)		Molar ratio $\frac{M_1^0}{M_2^0}$	Benzoyl peroxide concentration c (%)	Yield of copolymer (%)	Mean rate of process divided by $\sqrt{c}$
M_1^0	M_2^0				
1.8957	0.1895	10.00	—	—	—
1.8975	0.1893	10.02	0.1	2.11	6.60
1.8980	0.1895	10.01	0.3	3.64	6.62
1.8966	0.1892	10.03	0.5	4.77	6.73
1.9112	0.1895	10.08	1.0	6.69	6.69
1.9368	0.1896	10.21	2.0	9.47	6.69
1.1000	0.5463	2.01	—	0.80	—
1.1080	0.5468	2.03	0.1	1.51	4.73
1.1018	0.5466	2.02	0.3	2.67	4.82
1.1213	0.5462	2.05	1.0	4.91	4.91
1.1798	0.5467	2.16	2.0	6.58	4.65
0.7358	0.7157	1.03	—	1.51	—
0.7187	0.7154	1.00	0.1	2.90	9.07
0.7197	0.7158	1.01	0.3	5.05	9.18
0.7280	0.7157	1.02	0.5	6.64	9.35
0.7205	0.7158	1.01	1.0	8.98	8.98
0.7292	0.7155	1.02	2.0	12.76	9.02

ethyl acetate, whereas copolymers having vinylcarbazole contents of up to 10 mole-% were soluble in methanol, ethanol, and acetic acid. A comparison of the dissolving powers of solvents for vinyl acetate-vinylcarbazole copolymers was carried out as follows [4]: 50 mg of the copolymer was dissolved in 2 ml of solvent, and the solution was "titrated" with nonsolvent (petroleum ether) at 20°. The end point was determined by comparison of the turbidity formed with the turbidity of a standard sample prepared by mixing 2 ml of 0.001 N $AgNO_3$ with 1 ml of N NaCl acidified with nitric acid. The number of milliliters of petroleum ether required was taken to be the precipitation value. This method made it possible at the expense of very little material, to find the variation of the solubilities of the copolymers with composition and to show which were the best solvents. The results are given in Fig. 3. It was found that dioxane and chloroform are the best solvents for vinyl acetate-vinylcarbazole copolymers.

Intrinsic Viscosity of Copolymer Solutions. In the viscosimetric determination of molecular weight, the most comprehensive and satisfactory relationship that has yet been found is $[\eta] = kM^a$ [5], in which $[\eta]$ is the intrinsic viscosity, k is a coefficient which is constant in a given polymer homologous series in a given solvent, and a is a quantity that characterizes the form of the macromolecule in solution. The value of a depends on the flexibility of the chains and varies from 0.5 to 2.

The intrinsic viscosity of a polymer solution depends on the nature of the solvent, but for a given solvent it rises with increase in the molecular weight of the polymer. Although the viscosimetric method does not enable us to obtain absolute values for the molecular weights of polymers of various classes (since the values of k and a are not known) – particularly of copolymers – nevertheless, the method does enable us to compare and characterize macromolecular substances. In our viscosity study we used solutions of vinyl acetate-vinylcarbazole copolymers in benzene at concentrations of 0.2, 0.4, and 0.8 g per 100 ml of solvent. Immediately before the measurements the solutions were filtered through a No. 2 glass filter to remove small specks. The measurements were carried out in an Ostwald viscometer at 20°. The temperature in the 30-liter thermostatic water bath was maintained constant within ± 0.001° with the aid of a contact thermometer and electronic relay of the type designed by Sochevanov

[6]. The dimensions of the capillary of the viscometer were selected so that the time of flow for benzene was not less than 90 seconds. Each measurement was repeated at least five times, and only those results which agreed within 0.2 second were taken into account. In order to keep a check on the cleanliness of the capillary, control measurements were made on pure benzene at definite intervals of time. Values of reduced viscosity (η_{sp}/c) were graphed against concentration, and the curves were extrapolated to zero concentration in order to give the intrinsic viscosity $[\eta]$ [7].

Fig. 4 shows that an addition of even a small amount of vinylcarbazole (about 20 mole-%) to vinyl acetate greatly reduces the molecular weight of the reaction products. All of the copolymers of vinyl acetate and vinylcarbazole have lower intrinsic viscosities than that of polyvinylcarbazole prepared under the same conditions. Our experimental results are in accord with the suggestion that we made [1] concerning the lowering of the molecular weight of the reaction products in the copolymerization of monomers of the vinylcarbazole type with vinyl esters.

Vitrification Temperature. The vitrification temperatures of vinyl acetate-vinylcarbazole copolymers of various compositions were determined by the dilatometric method, in which the point of inflection (T_v) is determined on the curve for volume against temperature. The compressed sample (1 g) was placed in a tube, which was then connected through the ground joint at its open end to a capillary 50 cm in length and 0.5 mm in internal diameter. The dilatometer was evacuated, and then filled with mercury up to a definite level in the capillary. In order to determine the volume as a function of temperature, the dilatometer was placed in a thermostat heated at a rate of 1° per minute over a period of five minutes. In the succeeding five minutes the temperature was maintained constant, and the height of the mercury column in the capillary was then read. The results of these experiments are shown in Fig. 5.

Fig. 5 shows that for vinyl acetate-vinylcarbazole copolymers the vitrification temperature varies with composition. The introduction of a little vinylcarbazole (3-10 mole-%) results in a lowering of T_v below that of polyvinyl acetate, whereas copolymers of low vinyl acetate content have vitrification temperatures that are even higher than that of polyvinylcarbazole.

It is known that the proportion of polar groups and atoms present in the polymer molecule, the nature of these groups, and the possibility of more or less close packing determine the forces of interaction between the macromolecular chains. Polyvinyl acetate contains the polar groups $-OCOCH_3$ having a molecular cohesion of 5600 cal/mole, and polyvinylcarbazole has nonpolar carbazole groups having a high molecular cohesion on account of the large number of $=CH-$ groups present in the molecule. Moreover, the polyvinylcarbazole molecules are arranged so that interaction must occur between the planes, and not the edges, of the hexagons, and the bonding energy is very high. Polyvinylcarbazole, therefore, has a higher vitrification temperature than polyvinyl acetate.

The lowering of the vitrification temperature of copolymers containing only a small amount of vinylcarbazole may be explained by a loosening of the packing of the chains and a reduction of the forces of interaction between chains arising from the introduction of large vinylcarbazole molecules into the polyvinyl acetate chains. The forces of interaction between carbazole groups do not then make up for the lowering of the energy of dipole linkages ($-OCOCH_3$) between chains.

The rise in the vitrification temperature of copolymers containing only a small proportion of vinyl acetate molecules is probably to be explained by steric effects that prevent the complete interaction of the carbazole groups of the polyvinylcarbazole chains. On this account the introduction of a few acetic ester groupings into the polyvinylcarbazole molecule will facilitate the rotation of monomer units about carbon-carbon bonds and lead to a more complete approach of the planes of the carbazole groups of the chains. The consequence of this is a rise in the vitrification temperature. Similar rises in the vitrification temperatures of copolymers, as compared with those of the homopolymers, was observed by Margaritova and Raiskaya [8] for the systems butadiene-dinonyl maleate and butadiene-dinonyl fumarate.

SUMMARY

1. A study was made of the effect of the initial ratio of components, the reaction temperature, and the initiator concentration on the rate of the copolymerization of vinyl acetate and vinylcarbazole.

2. Vinyl acetate-vinylcarbazole copolymers of various compositions prepared at 100° were characterized. It was shown that the solubilities, molecular weights, and vitrification temperatures of copolymers prepared under identical conditions are dependent on composition.

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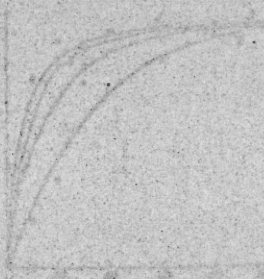

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 91. TRANSARYLATION OF BIBENZYL AT VARIOUS TEMPERATURES

G. S. Kolesnikov and V. V. Korshak

We have previously shown that, in presence of aluminum chloride, bibenzyl and other diarylalkanes undergo a linear-polycondensation reaction, which we have called transarylation [1-3]. We considered that it was desirable to determine the main laws governing this reaction, and therefore undertook a more detailed study of the transarylation of bibenzyl. We selected bibenzyl for study because in this case the probability of the occurrence of an intramolecular cyclization reaction is practically zero and the course of the main process will therefore not be distorted by it, as it might be in the transarylation of, for example, diphenylmethane. In the present paper we present our results on the transarylation of bibenzyl at various temperatures.

The experimental procedure was as follows. A weighed amount of bibenzyl was placed in a test tube provided with a side tube and was heated in a bath of glycerol or Wood's metal, which was maintained at a constant temperature. The tube was closed with a stopper through which passed a thermometer and a bubbling tube that reached almost to the bottom of the test tube. When the bibenzyl reached the desired temperature and was found to undergo no further change in the course of 15-20 minutes, finely ground aluminum chloride was introduced into the tube, care being taken to prevent the aluminum chloride from falling on the sides of the tube. Immediately after this addition, the stopper with the thermometer and bubbling tube was replaced and dry nitrogen was passed through the reaction mixture at 40 ml/minute. The side tube of the reaction vessel was connected to a water-cooled condenser and a receiver graduated accurately within 0.1 ml. The reaction time was reckoned from the time when the aluminum chloride was added to the bibenzyl.

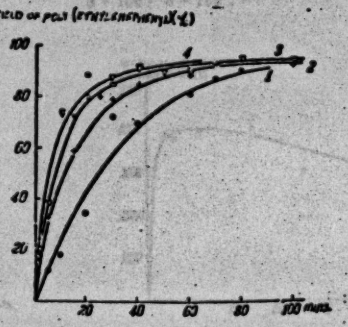

Fig. 1. Transarylation of bibenzyl at various temperatures: 1 - 80°; 2 - 90°; 3 - 100°; 4 - 105°.

After the addition of aluminum chloride the reaction mixture immediately darkened and foamed as a result of the evaporation of the benzene formed; the bulk of the benzene collected in the receiver in the first 20-40 minutes. At the end of the prearranged period for the particular experiment, the test tube was taken from the heating bath, dilute hydrochloric acid and benzene were added as quickly as possible, and the contents of the test tube were transferred quantitatively to a separating funnel with the aid of benzene. The aqueous layer was separated from the benzene solution, which was washed several times with water and dried with calcium chloride. The calcium chloride used for drying was washed with two small portions of dry benzene, and this benzene was added to the main benzene solution. Benzene was distilled off, bibenzyl was distilled off under reduced pressure, and the residue was weighed.

When, apart from soluble poly(ethylenephenyl), an insoluble three-dimensional polycondensation product was formed, the contents of the reaction vessel were transferred quantitatively to a conical flask, and the whole mixture was filtered through a sintered-glass filter under suction. The insoluble product was washed with benzene until the washings were no longer colored, and it was then dried and weighed. The washings were added to the filtrate, which was treated as indicated above.

In order to determine the effect of temperature on the rate of the transarylation of bibenzyl, four series

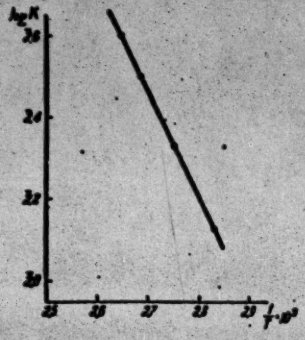

Fig. 2. Effect of temperature on the rate of the transarylation of bibenzyl.

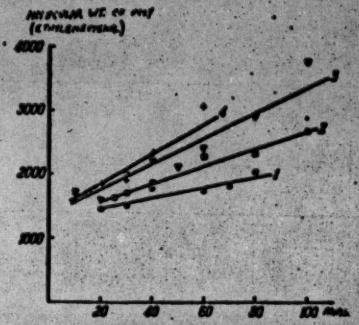

Fig. 3. Effect of the reaction temperature on the molecular weight of poly(ethylenephenyl): 1 - 80°; 2 - 90°; 3 - 100°; 4 - 105°.

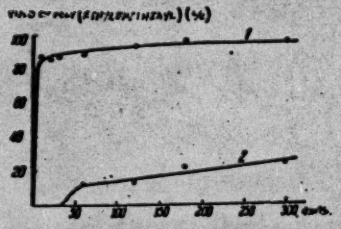

Fig. 4. Transarylation of bibenzyl at 140°; 1 - total yield; 2 - yield of three-dimensional product.

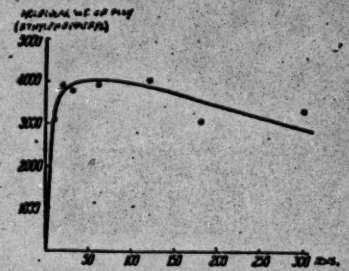

Fig. 5. Transarylation of bibenzyl at 140°.

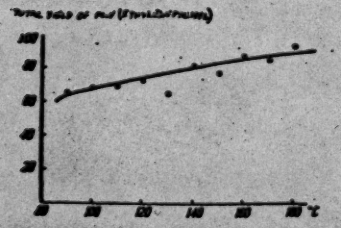

Fig. 6. Transarylation of bibenzyl at various temperatures.

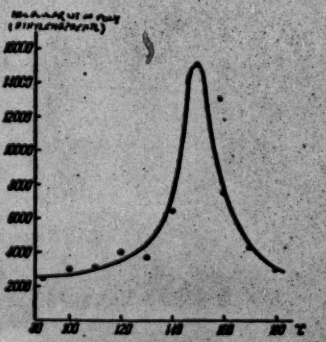

Fig. 7. Effect of reaction temperature on the molecular weight of poly(ethylenephenyl).

of experiments were carried out at various temperatures. In all the experiments of these series the aluminum chloride concentration was constant at 6.8 mole-%. In the experiments of a given series the temperature was kept constant. The results of these experiments are presented in Tables 1-4 and Fig. 1. The rate constants for the transarylation reaction were calculated from the usual formulas:

$$K_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$K_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)},$$

in which a is the maximum yield of poly(ethylenephenyl) that is theoretically possible (on the assumption that each bibenzyl molecule is converted into $-C_6H_4CH_2CH_2-$) (in basal moles); x is the amount of poly(ethylenephenyl) formed (basal moles); and t is time (seconds). The dimensions of the second-order rate constant will be $sec^{-1}mole^{-1}$, for each basal mole of poly(ethylenephenyl) formed corresponds to one mole of bibenzyl that has undergone reaction.

In the separation of the reaction products we isolated the unchanged bibenzyl, but part of it was lost owing to incomplete condensation during distillation. We were therefore obliged to have recourse to the units of measurement indicated above.

It will be seen from Tables 1-4 that the transarylation reaction is governed by the laws of a second-order reaction. At 90°, 100°, and 105°, the rate constant calculated for a first-order reaction diminishes with time; at 80° this "constant" is indeed constant, probably because of the low concentration of growing chains at this temperature, which results in a quasiunimolecular reaction. Moreover, the poly(ethylenephenyl) formed probably reacts with benzene, which is somewhat difficult to remove from the reaction mixture at 80°. At 80° the second-order rate constant rises at first and then remains constant. At 80°, for times not less than 30 minutes, the mean second-order constant is $13.5 \cdot 10^{-3}$, and for 90°, 100° and 105° the mean second-order constants are $21.5 \cdot 10^{-3}$, $31.5 \cdot 10^{-3}$, and $40.0 \cdot 10^{-3}$, respectively. On the basis of these values, the temperature coefficients of the reaction rates are:

TABLE 1

Transarylation of Bibenzyl at 80°

Duration of experiment (minutes)	Yield of poly(ethylenephenyl) (%)	$K_1 \cdot 10^4$	$K_2 \cdot 10^3$	Molecular weight of poly(ethylenephenyl)
5	12.3	4.4	4.2	Products of low molecular weight
10	18.4	3.4	3.4	
20	34.5	3.5	4.0	1450
30	72.8	7.2	13.4	1520
40	70.0	5.0	8.9	1770
60	81.4	4.7	11.1	1690
70	88.0	5.0	13.8	1760
80	91.0	5.1	18.4	2030

TABLE 2

Transarylation of Bibenzyl at 90°

Duration of experiment (minutes)	Yield of poly(ethylenephenyl) (%)	$K_1 \cdot 10^4$	$K_2 \cdot 10^3$	Molecular weight of poly(ethylenephenyl)
5	33.2	13.5	15.1	Products of low molecular weight
15	58.6	9.8	14.3	
25	80.1	10.7	24.3	1630
30	79.2	8.7	19.2	1690
40	85.3	8.0	22.0	1850
60	89.3	6.2	21.0	2270
80	93.6	5.7	27.8	2290
100	94.9	5.0	28.4	2650

TABLE 3

Transarylation of Bibenzyl at 100°

Duration of experiment (minutes)	Yield of poly(ethylenephenyl) (%)	$K_1 \cdot 10^4$	$K_2 \cdot 10^3$	Molecular weight of poly(ethylenephenyl)
5	38.5	16.2	19.0	—
10	73.5	22.1	42.0	1730
15	72.2	14.2	28.2	1680
20	80.1	13.4	30.4	1570
30	84.8	10.5	28.3	1980
40	91.5	10.2	40.4	2190
50	90.2	4.9	27.7	2120
60	90.2	6.4	21.3	2370
80	96.3	7.1	48.5	2910
100	95.4	5.1	31.2	3740

$$\frac{K_{90}}{K_{80}} = 1.59;\ \frac{K_{100}}{K_{90}} = 1.47;\ \frac{K_{110}}{K_{100}} = 1.53;\ \frac{K_{120}}{K_{110}} = 1.61;$$

the mean value being 1.54 ± 0.07. The activation energy, calculated from these rate constants, is 11,400 ± 500 cal/mole (Fig. 2).

TABLE 4

Transarylation of Bibenzyl at 105°

Duration of experiment (minutes)	Yield of poly(ethylenephenyl) (%)	$K_1 \cdot 10^4$	$K_2 \cdot 10^3$	Molecular weight of poly(ethylenephenyl)
10	74.4	22.7	44.0	1710
20	88.8	18.3	60.7	1830
30	84.9	10.5	28.2	1880
40	91.9	10.5	42.8	2240
60	91.0	6.4	24.5	3080

The molecular weight of the poly(ethylenephenyl) formed in the transarylation of bibenzyl in presence of aluminum chloride depends on the reaction temperature. It will be seen from Tables 1-4 and Fig. 3 that raising of the transarylation temperature results in a rise in the molecular weight of the poly(ethylenephenyl), which is not very noticeable in the early stages of reaction, but is quite obvious in the later stages. From Tables 1-4 and Figures 1 and 3 it can be seen also that the rise in the molecular weight of poly(ethylenephenyl) is more rapid in the second half of the process than the rise in the

TABLE 5

Transarylation of Bibenzyl at 140°

Duration of experiment (minutes)	Yield (%) of soluble poly(ethylenephenyl)	Yield (%) of three-dimensional poly(ethylenephenyl)	Molecular weight of poly(ethylenephenyl)
10	86.6	—	3120
20	85.8	—	3890
30	87.5	—	3788
60	77.0	12.3	3960
120	80.5	13.1	4040
180	75.3	21.9	3110
300	75.3	23.9	3200

TABLE 6

Transarylation of Bibenzyl at Various Temperatures

Temperature (°C)	Yield (%) of soluble poly(ethylenephenyl)	Yield (%) of three-dimensional poly(ethylenephenyl)	Molecular weight of poly(ethylenephenyl)
90	64.8	—	2480
100	68.3	—	3020
110	70.0	—	3100
120	74.4	—	4000
130	61.3	4.4	3680
140	70.0	13.1	7440
150	63.0	15.8	15070
160	67.4	21.9	7550
170	61.3	28.2	4300
180	71.8	24.5	3130

actual yield of poly(ethylenephenyl). This indicates, that in addition to the gradual rise in the molecular weight of the poly(ethylenephenyl) resulting from its reaction with bibenzyl, products of higher molecular weight are formed by reaction of poly(ethylenephenyl) molecules among themselves.

In order to determine the variation of molecular weight in the course of the transarylation of bibenzyl at higher temperatures, we carried out a series of experiments at 140° in presence of 6.8 mole-% of aluminum chloride. The results are given in Table 5 and in Figures 4 and 5.

It will be seen from Table 5 and Figures 4 and 5 that at 140° the transarylation of bibenzyl results in the formation of soluble poly(ethylenephenyl) and an insoluble, infusible, three-dimensional polycondensation product, the yield of which rises with increase in the duration of the reaction. It is interesting to note that the molecular weight of the soluble poly(ethylenephenyl) rises rapidly at first, attains a maximum value, and then immediately begins to fall; simultaneously the yield of three-dimensional polycondensation products rises. In our opinion, this fall in molecular weight is to be explained by the removal of the longest linear molecules, which participate preferentially in the cross-linking that results in the formation of the three-dimensional products; as we have shown previously [4], the probability of branching, and therefore the probability of participation in the formation of three-dimensional molecules, rises with increase in the length of the molecules of

linear condensation products.

We studied also the effect of temperature on the molecular weight of the transarylation products from bibenzyl over the range 90-180° for a constant aluminum chloride concentration of 6.8 mole-% and a constant duration of reaction of five hours. The results are given in Table 6 and Figures 6 and 7.

Table 6 shows that rise of transarylation temperature results in the formation of three-dimensional product, the yield of which rises with rise in temperature. The molecular weight of the soluble poly(ethylenephenyl) increases at first, attains a maximum of 150°, and then rapidly diminishes (Fig. 7). In our opinion, this fall in molecular weight is due to the formation of three-dimensional products from the poly(ethylenephenyl) of highest molecular weight. It is quite probable that at 160-180° the poly(ethylenephenyl) of highest molecular weight reacts simultaneously with the polycondensation products of lower molecular weight and with the bibenzyl that has not yet reacted. As a result of these reactions, the molecular weight of the soluble poly(ethylenephenyl) falls.

SUMMARY

1. The transarylation of bibenzyl in presence of aluminum chloride was studied at various temperatures.

2. It was found that the transarylation of bibenzyl is subject to the laws of a second-order reaction, the activation energy being 11,400 ± 500 cal/mole.

3. It was shown that, in the transarylation of bibenzyl, chain growth occurs not only as a result of the reaction of poly(ethylenephenyl) with bibenzyl, but also as a result of the reaction of poly(ethylenephenyl) molecules among themselves.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 92. EFFECT OF CATALYST CONCENTRATION ON THE TRANSARYLATION OF BIBENZYL

G.S. Kolesnikov and V.V. Korshak

In our previous communication we showed the effect of temperature on the transarylation of bibenzyl and we established that this reaction is subject to the laws of a second-order reaction [1]. We had previously shown that the aluminum chloride concentration is not a matter of indifference in the polycondensation of 1,2-dichloroethane with benzene, and it would be expected that in the transarylation of bibenzyl the aluminum chloride concentration would again affect the course of the process and the molecular weights of the reaction products [2]. In the present paper we give the results of experiments carried out with the object of verifying this supposition.

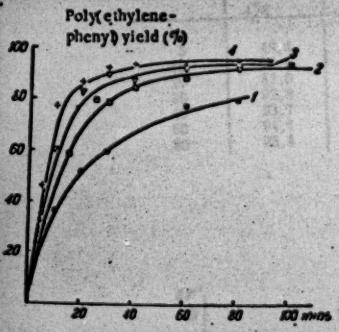

Fig. 1. Transarylation of bibenzyl at different aluminum chloride concentrations: 1 - 3.4 mole-%; 2 - 6.8 mole-%; 3 - 10.2 mole-%; 4 - 13.6 mole-%.

TABLE 1

Transarylation of Bibenzyl at an Aluminum Chloride Concentration of 3.4 mole-%

Duration of reaction (minutes)	Yield of poly(ethylenephenyl) (%)	$K_2 \cdot 10^3$	Molecular weight of poly(ethylenephenyl)
10	36.3	8.7	—
20	51.6	8.1	1430
30	59.9	7.6	1520
60	78.3	9.1	1640
80	81.4	8.3	1660

In order to determine the effect of catalyst concentration on the rate of the transarylation of bibenzyl, four series of experiments were carried out at 90° for different concentrations of aluminum chloride. The results are presented in Tables 1-4 and Fig. 1. As it has already been established [1] that the transarylation of bibenzyl is governed by the laws of a second-order reaction, only second-order constants were calculated. The experimental procedure was the same as before [1].

The mean values of the rate constants for the transarylation of bibenzyl at aluminum chloride concentrations of 3.4, 6.8, 10.2, and 13.6 mole-% are $8.4 \cdot 10^{-3}$, $21.5 \cdot 10^{-3}$, $32.9 \cdot 10^{-3}$, and $46.9 \cdot 10^{-3}$ respectively. These results show that the rate constant for the reaction is directly proportional to the concentration of the catalyst, aluminum chloride (Fig. 2).

It will be seen from Tables 1-4 and Fig. 3 that the molecular weight of the poly(ethylenephenyl) rises with increase in the catalyst concentration and the rise in molecular weight in the second half of the process is more rapid than the increase in yield. This indicates that the formation of poly(ethylenephenyl) proceeds not

TABLE 2

Transarylation of Bibenzyl at an Aluminum Chloride Concentration of 6.8 mole-%

Duration of reaction (minutes)	Yield of poly(ethylenephenyl) (%)	$K_0 \cdot 10^5$	Molecular weight of poly(ethylenephenyl)
5	33.2	15.1	Products of low molecular weight
15	58.6	14.3	
25	80.1	24.3	1630
30	79.2	19.2	1690
40	85.3	22.0	1850
60	89.3	21.0	2270
80	83.6	27.8	2290
100	94.9	28.4	2650

TABLE 3

Transarylation of Bibenzyl at an Aluminum Chloride Concentration of 10.2 mole-%

Duration of reaction (minutes)	Yield of poly(ethylenephenyl) (%)	$K_0 \cdot 10^5$	Molecular weight of poly(ethylenephenyl)
10	59.9	23.9	1550
20	82.7	36.2	1740
30	90.2	46.1	2100
40	88.4	28.8	1900
60	92.8	32.3	2250
80	94.1	30.0	2600

TABLE 4

Transarylation of Bibenzyl at an Aluminum Choride Concentration of 13.6 mole-%

Duration of reaction (minutes)	Yield of poly(ethylenephenyl) (%)	$K_0 \cdot 10^5$	Molecular weight of poly(ethylenephenyl)
5	46.4	26.2	1410
10	77.4	52.0	1600
20	87.0	51.0	1780
30	92.8	64.6	2180
40	93.7	55.6	2290
60	94.1	40.0	2610
80	95.4	39.0	2780

TABLE 5

Transarylation of Bibenzyl at 140° with Various Amounts of Catalyst

Catalyst concentration (mole-%)	Yield (%)		Molecular weight of soluble poly(ethylenephenyl)
	of soluble poly(ethylenephenyl)	of three-dimensional poly(ethylenephenyl)	
3.4	65.6	—	1520
6.8	58.6	13.1	10100
13.6	60.4	18.4	8580
20.4	56.9	24.9	6460
27.2	63.9	25.8	5790

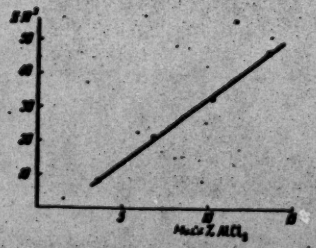

Fig. 2. Effect of the aluminum chloride concentration on the rate of the transarylation of bibenzyl.

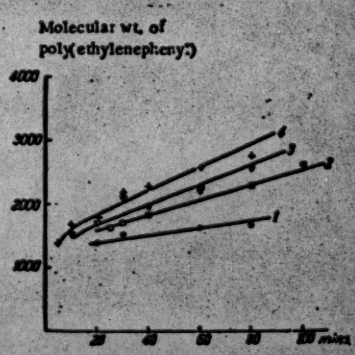

Fig. 3. Effect of the aluminum chloride concentration on the molecular weight of the poly(ethylenephenyl): 1 - 3.4 mole-%; 2 - 6.8 mole-%; 3 - 10.2 mole-%; 4 - 13.6 mole-%.

only as a result of reaction between growing poly(ethylenephenyl) molecules and bibenzyl, but also as a result of reaction of poly(ethylenephenyl) molecules among themselves [1].

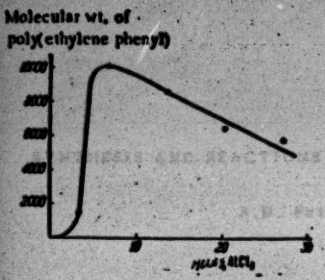

Fig. 4. Transarylation of bibenzyl at 140°.

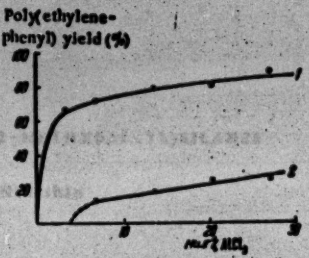

Fig. 5. Transarylation of bibenzyl at 140°: 1 - total yield; 2 - yield of three-dimensional product.

With the object of determining the effect of catalyst concentration on the molecular weight of poly(ethylenephenyl) formed in the transarylation of bibenzyl at a higher temperature, a series of experiments was carried out at 140° with varying amounts of catalyst, the duration of the reaction being kept constant for four hours. The results are presented in Table 5 and Figures 4 and 5.

It will be seen from Table 5 and Fig. 4 that, with increase in catalyst concentration, the molecular weight of the poly(ethylenephenyl) increases rapidly at first, but later there is a lowering of the molecular weight of the soluble poly(ethylenephenyl) with simultaneous increase in the yield of three-dimensional poly-(ethylenephenyl). The formation of three-dimensional transarylation products occurs mainly at the expense of the poly(ethylenephenyl) of highest molecular weight.

SUMMARY

A study wasmade of the effect of aluminum chloride concentration on the rate of the transarylation of bibenzyl and on the molecular weight of the poly(ethylenephenyl) formed.

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SYNTHESIS AND REACTIONS OF CHLORO(2-METHYLALLYL)SILANES

A.D. Petrov and G.I. Nikishin

In recent papers by Petrov and Mironov [1] and Petrov and Nikishin [2], the organomagnesium synthesis of some methyl(2-methylallyl)- and trichloro(2-methylallyl)silanes were described. On the other hand, the direct synthesis of chloro(2-methylallyl)silanes has not yet been studied, though some papers have appeared relating to the direct synthesis of other alkenylsilanes. Hurd [3] prepared vinyl- and allyl-chlorosilanes, and Petrov and Sadykh-Zade [4] prepared a whole range of chloro compounds containing one and two silicon atoms.

The direct synthesis of chloro(2-methylallyl)silanes would be of no less interest, if only because of the valuable properties which, according to the patent literature [5], are possessed by organosilicon polymers derived from monomers containing 2-methylallyl radicals. Among the products that we have prepared in the present investigation of the direct synthesis of chloro(2-methylallyl)silanes in a total yield of 40%, trichloro-(2-methylallyl)silane $Cl_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ predominated; the synthesis therefore differs in this respect from that of chloroisobutylsilanes, in which dichloroisobutylsilane $Cl_2HSiCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ predominated. The isolation of pure chloro(2-methylallyl)silanes was rendered difficult by the presence of diene hydrocarbons of similar boiling point; 2,5-dimethyl-1,5-hexadiene, formed evidently, by the combination of free 2-methylallyl radicals and partially isomerized under the conditions of the synthesis into 2,5-dimethyl-2,4-hexadiene.

Contrary to our expectations, attempts to methylate $(CH_3)_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ with excess of methylmagnesium chloride or iodide were unsuccessful. The main product was hexamethyldisiloxane, and only when methylmagnesium chloride was used was $(CH_3)_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ obtained also, the yield being only 3%:

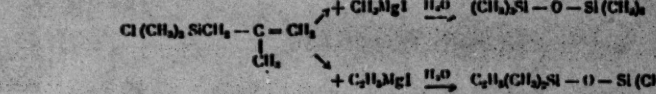
$$Cl_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2+CH_3MgI\xrightarrow{H_2O}(CH_3)_3Si-O-Si(CH_3)_3$$

and

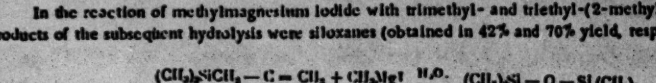
$$Cl_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2+CH_3MgCl\xrightarrow{H_2O}$$

$$\rightarrow (CH_3)_3Si-O-Si(CH_3)_3+(CH_3)_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

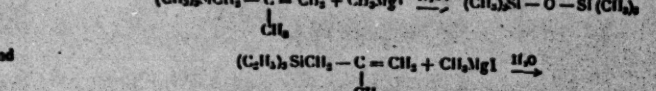
A less direct method for the synthesis of $(CH_3)_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ from $Cl(CH_3)_2SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ and excess of methylmagnesium chloride (though a smaller excess than in the case of $Cl_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$) gave the desired compound as the main product, although again the replacement of methyl chloride by methyl or ethyl iodide resulted in the isolation of only siloxanes:



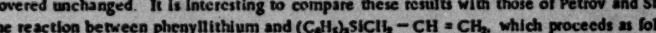
In the reaction of methylmagnesium iodide with trimethyl- and triethyl-(2-methylallyl)silanes, the main products of the subsequent hydrolysis were siloxanes (obtained in 42% and 70% yield, respectively).



and

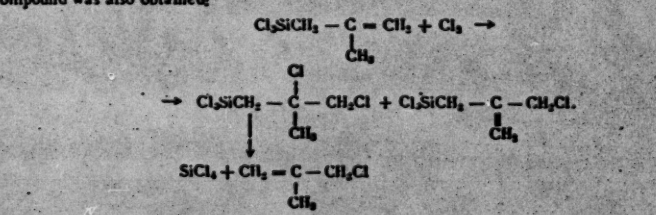


In the case of triethyl(2-methylallyl)silane, the 2-methylpropene that was isolated was identified in the form of 1,2-dibromo-2-methylpropane. When $(C_2H_5)_3SiCH_2-CH=CH_2$ was treated with methylmagnesium iodide and the product hydrolyzed, breakdown at the Si-C link did not occur and allyltriethylsilane was recovered unchanged. It is interesting to compare these results with those of Petrov and Shchukovskaya [6] on the reaction between phenyllithium and $(C_6H_5)_3SiCH_2-CH=CH_2$, which proceeds as follows:

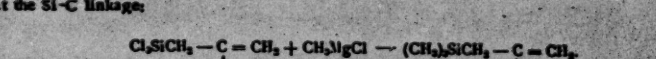


Hence, with respect to their effectiveness in attacking allylsilanes, we may place the nucleophilic reagents studied in the following order: $C_6H_5Li > CH_3MgI > CH_3MgCl$.

In order to make a further study of condensation reactions with RMgX, we then carried out the chlorination of $Cl_3SiCH_2-C(CH_3)=CH_2$ in the hope that the main reaction would be Lvov-Tishchenko anomalous chlorination. Our hopes were realized: in addition to the dichloride (which underwent β-breakdown), a monochloro compound was also obtained:



Methylation of this monochloro derivative with methylmagnesium chloride occurred without breakdown at the Si-C linkage:



Hence, the strength of the Si-C linkage with respect to the action of nucleophilic reagents is lower in $(CH_3)_3Si-CH_2-C(CH_3)=CH_2$ than in $(C_2H_5)_3SiCH_2CH=CH_2$ and $(CH_3)_3SiCH_2-C(CH_2Cl)=CH_2$. The strengthening of the Si-C bond by the introduction of chlorine into the 2-methylallyl radical is probably to be explained by a reduction in the polarity of the Si-C bond, which approaches the C-C bond in character and becomes inert both to

products of the hydrolysis of Grignard reagents and also to the reagents themselves.

It should be noted that, as shown in separate experiments, boiling with 5% or 10% aqueous caustic potash does not break the Si-C bond in triethyl(2-methylallyl)silane. Hence, the above-mentioned breakdown of this compound with formation of 2-methylpropene is not due to the action of alkaline hydrolysis products. It is evident that the Grignard reagent and the alkenylsilane form some sort of complex, which is hydrolyzed by water.

EXPERIMENTAL

Chloro(2-methylallyl)silanes. 2-Methylallyl chloride was passed at 30 g per hour through a glass tube (length 600 mm, diameter 40 mm) filled with pieces of Si-Cu alloy (80% Si, 20% Cu) and mounted in an electric tube furnace, which maintained the temperature at 330 ± 10°. The reaction products were condensed with a water condenser. From 906 g (10 moles) of 2-methylallyl chloride, 726 g of condensate was obtained, and fractionation of this through a column (1100 mm in height, and filled with glass rings, 3 mm in diameter) gave the following fractions:

Fraction	I, B.p	30-100°; 114 g;	15.7%
Fraction	II, B.p	100-115°; 8 g;	1.1%
Fraction	III, B.p.	115-122°; 95 g;	13.2%
Fraction	IV, B.p.	122-135°; 23 g;	3.1%
Fraction	V, B.p.	135-140°; 166 g;	22.8%
Fraction	VI, B.p.	140-207°; 34 g;	4.7%
Fraction	VII, B.p.	207-213°; 32 g;	4.4%
	Residue	137 g;	18.9%

When refractionated, Fractions III, V, and VII yielded, respectively: dichloro(2-methylallyl)silane, trichloro(2-methylallyl)silane, and dichlorobis-2-methylallylsilane (for properties see Table), and also small amounts of 2,5-dimethyl-1,5-hexadiene (b.p. 113-114°; n_D^{20} 1.4314) from Fraction III and of 2,5-dimethyl-2,4-hexadiene (b.p. 133.5°; n_D^{20} 1.4738) from Fraction V. The total yield of chloro(2-methylallyl)silanes was 40%, i.e. was less than the yield of allylchlorosilanes obtained by Hurd [3], namely 60%.

Methylation of $Cl_3SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$. A stream of methyl chloride was passed through 700 ml of ether containing 40 g (1.64 moles) of magnesium until the whole of the metal had disappeared. Trichloro(2-methylallyl)silane, amounting to 72 g (0.38 mole), was added to the resulting organomagnesium compound. The mixture was boiled for five hours and then decomposed with water. Fractionation of the dried ethereal solution gave 12.2 g (39.5%) of hexamethyldisiloxane (b.p. 97-101°; n_D^{20} 1.3778; d_4^{20} 0.7623) (the literature [7] gives b.p. 99-100°; n_D^{20} 1.3771; d_4^{20} 0.7638) and 1.5 g (3%) of trimethyl(2-methylallyl)silane, b.p. 110.5-112°; n_D^{20} 1.4195; d_4^{20} 0.7436. When methyl iodide was used, only hexamethyldisiloxane could be isolated.

Methylation of $Cl_2HSiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$. All the succeeding methylations of various chloro(2-methylallyl)silanes with methyl chloride or iodide were carried out under identical conditions with excess of CH_3MgX. Reaction of 29 g (0.186 mole) of dichloro(2-methylallyl)silane and methylmagnesium chloride prepared from 8.24 g (0.75 mole) of magnesium gave 8.5 g (40%) of dimethyl(2-methylallyl)silane, b.p. 91-95°. In this synthesis no siloxane was obtained.

Preparation of $Cl(CH_3)_2SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$. A mixture of 64.5 g (0.5 mole) of dichlorodimethylsilane and 8 g (0.75 mole) of 2-methylallyl chloride was added over a period of six hours to 24.32 g (1 mole) of magnesium in 1.2 liters of ether. When the addition was complete, the mixture was boiled for four hours. The precipitate was filtered off, and fractionation of the ethereal solution gave 33.4 g (44.9%) of chlorodimethyl(2-methylallyl)-silane, b.p. 130-134°, and 7.6 g (9%) of dimethylbis-2-methylallylsilane, b.p. 176-179° and n_D^{20} 1.4556. The properties of chlorodimethyl(2-methylallyl)silane are given in the table.

Methylation of $Cl(CH_3)_2SiCH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$. Reaction between methylmagnesium chloride, prepared from

Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Analysis (%)
$Cl_2HSiCH_2-C(CH_3)=CH_2$	119.5 (743)	1.4460	1.0673	38.81	38.50	Found H 5.29; 5.23; C 31.29; 31.17; Cl 44.95; 44.80; Si 17.68; 17.80
						Calculated H 5.19; C 30.97; Cl 45.72; Si 18.09
$Cl_3SiCH_2-C(CH_3)=CH_2$	139 (743)	1.4533	1.1090	42.75	42.59	Found H 4.07; 4.27; C 26.30; 26.36; Cl 56.86; 57.00
						Calculated H 3.72; C 26.16; Cl 56.14
$Cl_2Si(CH_2-C(CH_3)=CH_2)_2$	210—211 (755)	1.4805	1.0566	56.28	56.36	
$Cl_3SiCH_2-C(CH_2Cl)=CH_2$	188—189 (746)	1.4846	1.3473	47.50	47.43	Found H 2.58; 2.78; C 21.44; 21.12; Cl 62.97; 62.95; Si 12.36; 12.43
						Calculated H 2.69; C 21.45; Cl 63.31; Si 12.53
$(CH_3)_2HSiCH_2-C(CH_3)=CH_2$	94.5—95 (749)	1.4190	0.7318	39.42	39.33	Found H 12.55; 12.50; C 62.96; 63.17; Si 24.58; 24.74
						Calculated H 12.36; C 63.08; Si 24.56
$(CH_3)_2SiCH_2-C(CH_3)=CH_2$	111—111.5 (758)	1.4193	0.7397	43.81	43.70	Found H 12.46; 12.44; C 65.88; 65.73; Si 21.97; 21.87
						Calculated H 12.57; C 65.54; Si 21.90
$(CH_3)_2SiCH_2-C(CH_2Cl)=CH_2$	162—163 (768)	1.4510	0.8900	48.75	48.54	Found H 9.33; 9.15; C 51.52; 51.64; Cl 21.66; 21.81; Si 17.19; 17.14
						Calculated H 9.29; C 51.67; Cl 21.79; Si 17.24
$Cl(CH_3)_2SiCH_2-C(CH_3)=CH_2$	133—134 (741)	1.4372	0.9068	43.00	43.33	

8.08 g (0.33 mole) of magnesium, and 25 g (0.17 mole) of chlorodimethyl(2-methylallyl)silane yielded 8.1 g (40%) of trimethyl(2-methylallyl)silane, b.p. 111-112° (see table). A very small amount of hexamethyldisiloxane (5%) was obtained. When methylmagnesium iodide was used, only hexamethyldisiloxane (b.p. 97-100°, n_D^{20} 1.3779; d_4^{20} 0.7633; yield 55%) was obtained.

Found %: C 45.63; H 11.17
Calculated %: C 44.4 ; H 11.17

Ethylation of $Cl(CH_3)_2SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$. Reaction between ethylmagnesium iodide, prepared from 7.3 g (0.3 mole) of magnesium, and 22.3 g (0.15 mole) of chlorodimethyl(2-methylallyl)silane gave 4.6 g (32%) of a product boiling over the range 149-151° (n_D^{20} 1.4008; d_4^{20} 0.7972). For $C_2H_5(CH_3)_2Si-O-Si(CH_3)_2C_4H_7$ the literature [8] gives b.p. 148° (751); n_D^{20} 1.4014; d_4^{20} 0.7995. No silahydrocarbons were obtained.

Chlorination of $Cl_3SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$. The chlorination of 83 g of trichloro(2-methylallyl)silane was carried out in ultraviolet radiation in the apparatus described by Ponomarenko and Moronov [3]; the treatment was continued until the boiling point of the liquid in the flask attained 176° (8 hours 15 minutes). Fractionation of the reaction mixture yielded 10 ml of silicon tetrachloride (b.p. 58-60°), 8 ml of 2-methylallyl chloride (b.p. 70-72°; n_D^{20} 1.4280), 31.5 g of unchlorinated trichloro(2-methylallyl)silane, and 19.1 g of a substance boiling at 187.5-189.5° and obtained in 31.5% yield on the amount of trichloro(2-methylallyl)silane that reacted. The properties of the product are given in the table.

Methylation of $Cl_3SiCH_2-\underset{\underset{CH_2Cl}{|}}{C}=CH_2$. This structure is ascribed to the product on the basis of the known mechanism of the chlorination of 2-methylpropene and of the chlorination of 2-methylallyl chloride [10], in which $ClCH_2-\underset{\underset{CH_2}{|}}{C}-CH_2Cl$ was obtained. Reaction between methylmagnesium chloride prepared from 10 g (0.41 mole) of magnesium, and 18 g (0.08 mole) of $Cl_3SiCH_2-\underset{\underset{CH_2Cl}{|}}{C}=CH_2$ gave 7.75 g (59.5%) of [2-(chloromethyl)allyl]trimethylsilane, b.p. 160-164°, the properties of which are given in the table.

The structure of $(CH_3)_3SiCH_2-\underset{\underset{CH_2Cl}{|}}{C}=CH_2$ (I) was confirmed also by a study of its Raman spectra, which was carried out by Egorov. The presence of the lines 1415, 1631, and 3087 cm^{-1} indicated the terminal position of the C=C bond [11, 12]. The choice, therefore, can be only between formulas (I) and $(CH_3)_3SiCHCl-\underset{\underset{CH_2}{|}}{C}=CH_2$ (II). This coice suggests a comparison with the spectrum of $(CH_3)_3SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$ (III). In this last compound frequencies of 1396 and 1415 cm^{-1} are present and the C=C frequency is 1 38 cm^{-1}. In the monochloro compound under investigation frequencies in the range of 1380-1395 cm^{-1} are absent and the C=C frequency is lowered to 1631 cm^{-1}. Since the 1380-1395 cm^{-1} frequencies belong to a CH_3 group at a C=C bond, preference must be given to the form (I), in which such a group does not occur; moreover, this structure explains the lowering of the C=C frequency (effect of the chlorine atom).

Reactions of $(CH_3)_3SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$; $(C_2H_5)_3SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$ and $(C_2H_5)_3SiCH_2-CH=CH_2$ with Methylmagnesium Iodide. 7.45 g of trimethyl(2-methylallyl)silane, 22 g of triethyl(2-methylallyl)silane, or 12 g of allyltriethylsilane was added to ethereal methylmagnesium iodide (prepared from 3.12, or 6 g of magnesium, respectively). There were visible signs of reaction. The ether was distilled off, and the residue was heated at 70-85° for 7-8 hours. In the case of $(C_2H_5)_3SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$, the internal space of the apparatus was connected to the atmosphere through a trap cooled by a mixture of dry ice and acetone. The trap remained empty during the whole time of heating. The flask was cooled, the ether that had been distilled off was added, and the contents of the flask were decomposed with water. In the first case 2 g (42%) of hexamethyldisiloxane (b.p. 102-104°,

n_D^{20} 1.3917; d_4^{20} 0.7628)was isolated from the ether layer, and in the second case 11.3 g (70%) of hexaethyldisiloxane (b.p. 232-233°, n_D^{20} 1.5088; d_4^{20} 1.7670) was isolated. The liquid that collected in the trap during decomposition of the reaction mixture rapidly absorbed bromine, and the dibromide so formed (11% yield) had the following properties: b.p. 152°, n_D^{20} 1.5088, and d_4^{20} 1.7670; these properties correspond to 1,2-dibromo-2-methylpropane. The allyltriethylsilane was recovered unchanged after the operation.

SUMMARY

1. The direct synthesis of chloro(2-methylallyl)silanes was carried out for the first time. A total yield of 40% was obtained, and trichloro(2-methylallyl)silane accounted for more than half of this.

2. It was shown that in trialkyl(2-methylallyl)silanes the Si-C bond is more resistant to the action of Grignard reagents than in allylsilanes.

3. Lvov-Tishchenko anomalous chlorination of trichloro(2-methylallyl)silane was carried out for the first time, and it was shown that the introduction of a chlorine atom into the 2-methylallyl radical strengthens the Si-C bond and makes it incapable of being broken down under the action of Grignard reagents.

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ACTION OF DILUTE NITRIC ACID ON ISOLATED LIGNIN

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The first investigations on the action of dilute nitric acid on lignin were associated with the question of the delignification of raw material of vegetable origin. Very little study has been devoted to the nitration of isolated lignin with dilute nitric acid. There is a reference to the oxidation of "hydrochloric acid" lignin with hot dilute nitric acid, which was found to result in a loss of methoxyl groups and an increase in the content of acidic groups [1]; oxalic acid was formed simultaneously. Hachihama and Oshishi [2], who treated lignin isolated from sugar cane with 5% nitric acid at 100°, obtained a nitro product containing 3-4% of nitrogen.

It is known that heating of vegetable raw materials with dilute nitric acid not only nitrates the lignin, but also brings about the partial breakdown of the lignin molecule. Nitrated monomers are formed in small amount. Thus, the Japanese chemists Hachihama and Oshishi [2], in their treatment of sugar cane with dilute nitric acid, found that the following substances were present in admixture with the nitrolignin: 4-hydroxy-3--nitrobenzaldehyde, 4-hydroxy-3-nitrobenzoic acid, and 4-hydroxy-3,5-dinitrobenzaldehyde. K. Shinra and J. Shinra [3] isolated 4-hydroxy-3-nitrobenzaldehyde from the liquid obtained by the digestion of Graminaceae with nitric acid.

We considered it to be of interest to study the nitration of isolated lignin with dilute nitric acid at the boil.

EXPERIMENTAL

Samples of "hydrochloric acid" and "hydrolysis" lignins were used in the experiments. The "hydrochloric acid" lignin was isolated from pine chips by means of fuming concentrated hydrochloric acid, sp. gr. 1.21, in accordance with Willstätter's method. The "hydrolysis" lignin of the Leningrad Hydrolysis Works was ground in a ball mill, extracted with water, extracted twice with dichloroethane, and dried - first in the air, and then over phosphoric oxide. The composition of the "hydrochloric acid" lignin was C 60.30%; H 6.25%; OCH_3 15.50%. The composition of the "hydrolysis" lignin was C 62.78%; H 5.79%; OCH_3 10.00%. Nitration was effected with 3%, 5%, and 7% nitric acid at the boil.

A stirred mixture of 10 g of lignin and 400 ml of 3% nitric acid was heated to the boil. When boiling began the mixture was heated for a further 15-180 minutes. The first experiments did not give positive results: the lignin remained unchanged. In later experiments it was observed that when stirring was switched off during the heating of the reaction mixture oxides of nitrogen were rapidly formed and the whole mass then foamed up. After 20-30 minutes the foaming ceased. It is to be noted that the formation of oxides of nitrogen during the heating did not depend on the temperature, but generally occurred at 70-80°. It was frequently observed that the addition of sodium nitrite hastened the onset of reaction, whereas in presence of ammonium nitrate nitration of lignin by dilute nitric acid did not take place.

In this way nitrolignins were obtained in the form of light-yellow powders, which could be readily filtered off and washed with water. The filtrates, which were of a pale-brown color, contained mainly oxalic acid. The composition of the nitrolignin obtained from "hydrochloric acid" lignin was C 54.14%, H 4.75%. The composition of the nitrolignin obtained from "hydrolysis" lignin was C 49.67%, H 4.28%.

All of the samples were analyzed for nitrogen, methoxyl, and carboxyl contents. Methoxyl groups were determined by Zeisel's method. Carboxyl groups were determined by Purves' method [4]. The results are given in the table.

TABLE

Expt. No.	Nitrating agent*	Reaction temperature (°C)	Time after coming to boil (minutes)	Yield of nitrolignin (% of original)	Nitrogen content (%)	OCH_3 content (%)**	COOH content (%)***	Notes
			"Hydrochloric Acid" lignin					
1	3% HNO_3	98	15	99.90	1.89	–	3.07	Evolution of oxides of nitrogen was observed
2	Ditto	98-99	30	99.20	2.02	10.90	2.77	Ditto
3	"	98-99	60	92.90	1.98	10.70	3.67	"
4	"	98-100	180	89.60	2.27	10.00	4.51	"
			"Hydrolysis" lignin					
1	3% HNO_3	99.5	15	80.20	2.86	4.00	4.88	"
2	3% HNO_3 with addition of $NaNO_2$	98	15	70.27	3.05	5.70	4.84	"
3	7% HNO_3	96	15	80.80	2.55	3.50	4.49	"
4	Ditto	96	15	80.80	2.50	–	4.47	"
5	5% HNO_3	98	15	82.56	2.32	–	4.33	"
6	3% HNO_3	100	30	92.30	0.32	10.00	1.38	No oxides of nitrogen were evolved

* Bath ratio 1:40 for 3% HNO_3 and 1:20 for 7% HNO_3.
** OCH_3 content of "hydrochloric acid" lignin 15.3%, and of "hydrolysis" lignin 10.00%.
*** COOH content of "hydrochloric acid" lignin 0.68%, and of "hydrolysis" lignin 0.66%.

As will be seen from the table, in the experiments in which no evolution of oxides of nitrogen was observed, no nitration occurred and the lignin remained almost unchanged. In all of the experiments in which oxides of nitrogen were formed, nitration of the lignin occurred. The nitrogen content of the nitrolignins was 2-3%. The nitration of lignin was accompanied by partial loss of methoxyl groups: a loss of 24-30% for "hydrochloric acid" lignin, and a loss of 38-62% for "hydrolysis" lignin.

In all of the experiments in which oxides of nitrogen were formed, oxidation of the nitrolignin occurred with the formation of carboxyl groups. It is possible that the number of carboxyls formed was considerably greater, since the reaction conditions facilitated decarboxylation.

From the nitrolignins obtained we were able to isolate 4,6-dinitroguaiacol (Chemical Abstracts numbering) in 0.82% yield in the following way. Dry nitrolignin prepared under the conditions described above (100 g; nitrogen content 2-3%) was extracted in the cold with ether. The ether extract was dried, and the ether was distilled off. The dry residue, amounting to 1.80 g, was a pale-brown crystalline mass. Recrystallization from ethanol yielded 4,6-dinitroguaiacol, m.p. 122.5°, undepressed by admixture with synthetic 4,6-dinitroguaiacol.

Found % N 12.74
$C_7H_6O_6N_2$. Calculated % N 13.08

SUMMARY

1. A study was made of the nitration of "hydrolysis" lignin with dilute nitric acid (3%, 5%, and 7%) at the boil.

2. It was shown that under these conditions the nitrating agent was oxides of nitrogen. The nitrogen content of nitrolignins obtained under these conditions does not exceed 3.0%.

3. When lignin is nitrated with dilute nitric acid at the boil, the methoxyl content diminishes and the carboxyl content increases.

4. From the nitration products from "hydrochloric acid" and "hydrolysis" lignins oxalic acid was isolated, and also 4,6-dinitroguaiacol in 0.32% yield.

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BRIEF COMMUNICATIONS

CONDENSATION OF FERROCENE WITH ALDEHYDES

A.N. Nesmeyanov and I.I. Kritskaya

The publication of work by Weinmayr [1] on the condensation of ferrocene (dicyclopentadienyliron) with aldehydes prompted us to publish our results in this field, which were included in a paper read by A.N. Nesmeyanov at the Fourteenth International Congress on Pure and Applied Chemistry in June 1955, but which did not constitute a finished investigation.

The aromatic properties of ferrocene, which are evident in sulfonation reactions [1], in arylation reactions with diazo compounds [2], in acylation with acid anhydrides, acid chlorides, and silicoanhydrides of acids, and in metallation, including mercuration [3], are manifested also in its condensation with aldehydes. We have found that, in presence of concentrated sulfuric acid, ferrocene is able to react with aqueous formaldehyde and also with benzaldehyde. Reaction proceeds readily and rapidly at 65-75° and gives 65-75% yields of condensation products. The products contain two ferrocene nuclei, and they correspond in composition to dimethylenediferrocene and dibenzylidenediferrocene $(C_5H_4)_2$ $Fe(CHR)_2$ $Fe(C_5H_4)_2$, in which R = H or C_6H_5. In the reaction of ferrocene with benzaldehyde, the substance $(C_5H_4)_2$ Fe [$CH(C_6H_5)$] [CH (OH) (C_6H_5)] Fe (C_5H_4) (C_5H_5) is also obtained. The benzaldehyde reaction products differ in melting point; they differ also in their solubilities in acetone, and it was therefore possible to separate them. All of the reaction products were obtained in the oxidized form as ferricinium derivatives, and they were isolated in the crystalline state by reduction with stannous chloride.

For the same condensation Weinmayr employed anhydrous hydrofluoric acid, which is much less convenient. Moreover, in the reaction with benzaldehyde he obtained a single substance, to which he attributed two greatly differing melting points. According to our results, the two melting points correspond to two different substances.

All of our products are readily crystallized from dioxane and benzene and are less readily crystallized from acetone. They are orange in color and are oxidized after long standing in the air. Work on these compounds will be continued.

EXPERIMENTAL

Dimethylenediferrocene. A mixture of 7.2 g (0.04 mole) of ferrocene and 1.2 g (0.04 mole) of formaldehyde (4.2 g of a 40% aqueous solution) was cooled to − 15°, and it was stirred while 50 ml of 96% sulfuric acid, also cooled to − 15°, was added rapidly. Stirring with cooling was continued for 15 minutes; the mixture was then stirred further for 30 minutes at room temperature and for 1 hour 15 minutes at 65-75°. The solution, which was at first reddish brown, gradually became green. The reaction mixture was cooled to room temperature and poured into 250 ml of water. The black precipitate that formed was filtered off; it contained traces of unchanged ferrocene and probably also products of far-reaching oxidation of the molecule. Concentrated hydrochloric acid (30-40 ml) was added to the filtrate, and then stannous chloride in small portions. As soon as the first portions of stannous chloride were added, a precipitate began to form which, toward the end of the reduction, became pure yellow in color. The addition of the reducing agent was continued until the green color of the solution disappeared, and the mixture was then set aside at room temperature for two hours. The precipitate was filtered off, washed - first with water acidified with hydrochloric acid, and then with pure water - and dried. The precipitate was found to be soluble in benzene, chloroform, and dioxane - less soluble in acetone and alcohol; it could be purified by shaking the benzene solution with alumina and recrystallization from dioxane.

It melted at 191° in a sealed capillary. The yield was 65-75%. Its molecular weight, determined cryoscopically in benzene, was 377, the value calculated for dimethylenediferrocene being 398.

Found %: C 66.45; 66.62; H 5.57; 5.68; Fe 27.13; 27.02
$C_{22}H_{22}Fe_2$. Calculated %: C 66.71; H 5.09; Fe 28.20

The substance oxidized in the air.

Dibenzylidenediferrocene. This substance can be prepared and isolated under the same conditions. A mixture of 14.4 g (0.08 mole) of ferrocene and 4.24 g (0.08 mole) of benzaldehyde was prepared under cooling, and it was then heated at 65-70° for 90 minutes. The precipitate was reduced, washed, and dried, and the product was heated with successive portions of acetone until the solution obtained was almost colorless. The acetone solution contained dibenzylidenediferrocene together with traces of ferrocene. The dibenzylidenediferrocene was purified by shaking the acetone solution with alumina and recrystallization from dioxane or acetone. The melting point of dibenzylidenediferrocene was 218-220° (sealed capillary). The total yield of condensation products was 12.4-16.2 g (60-75%). The mixture of products contained about 50% of dibenzylidenediferrocene.

Found %: C 74.14; 73.91; H 5.71; 5.91; Fe 20.05; 19.80
$C_{34}H_{28}Fe_2$. Calculated %: C 74.47; H 5.14; Fe 20.37

The acetone-insoluble part of the precipitate was crystallized from dioxane or benzene (the solution was first shaken with alumina, which adsorbed oxidation products). It melted at 268-270° (sealed capillary). The product was probably an intermediate compound containing one hydroxy group.

Found %: C 72.50; 72.46; H 5.70; 5.82; Fe 19.82; 19.80
$C_{34}H_{30}Fe_2O$. Calculated %: C 72.11; H 5.34; Fe 19.73

When allowed to stand for a long time in the air, all three substances darken and acquire an impurity that is adsorbed by alumina, i.e. are oxidized.

SUMMARY

1. The reaction of ferrocene with aliphatic and aromatic aldehydes was studied.

2. It was shown that, in presence of concentrated sulfuric acid, ferrocene reacts with formaldehyde and with benzaldehyde with formation of a dimethylenediferrocene and dibenzylidenediferrocene, respectively. In the reaction with benzaldehyde a compound corresponding in composition to $(C_5H_4)_2$ Fe $[CH(C_6H_5)]$ $[CH(OH)(C_6H_5)]$ Fe $(C_5H_4)(C_5H_5)$ was also obtained.

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DIPOLE MOMENTS OF ALKYL 2-DIALKYLAMINOVINYL KETONES

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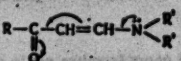
We have measured the dipole moments of some members of a class of unsaturated amino compounds $RCOCH = CHNR_2'$ synthesized by Kochetkov [1]. The polarities of these compounds may serve as a criterion for the conjugation of the carbonyl bond with the unshared electron pair of the nitrogen via the double bond. The shift of electrons may be represented by the formula:



As a result of the increase in the negative charge on the oxygen, the weakening of the double-bond character of the C=C bond, and the increase in the positive charge on the nitrogen, a considerable dipole moment should arise. It is of interest to compare the results of a physical method with the chemical behavior of these substances.

Dielectric constants were determined by the heterodyne-beat method in benzene solution at 25°. The refractions R_D were measured by Kochetkov. It is interesting that departures from additivity of 4-5 cc were here detected. Values of the total polarization P_∞, the refraction R_D, and the dipole moment μ are given in Table 1.

TABLE 1

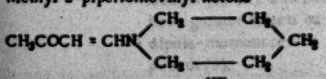
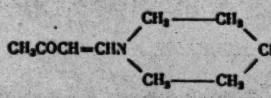
Substance	P_∞	R_D	$\mu \cdot 10^{18}$
2-Diethylaminovinyl methyl ketone $CH_3COCH = CHN(C_2H_5)_2$ (I)	715.40	47.26	5.67
Methyl 2-piperidinovinyl ketone  (II)	619.09	49.97	5.23
2-Dimethylaminovinyl methyl ketone $CH_3COCH = CHN(CH_3)_2$ (III)	570.74	37.38	5.06
2-Dimethylaminovinyl propyl ketone $CH_3CH_2CH_2COCH = CHN(CH_3)_2$ (IV)	532.10	47.18	4.83
2-Dimethylaminovinyl isobutyl ketone $(CH_3)_2CHCH_2COCH = CHN(CH_3)_2$ (V)	528.80	51.62	4.79

Table 2 gives the measured values of the mole fraction f, dielectric constant ϵ, density d, and the coefficients α and β of the Hedestrand equation.

TABLE 2

Formula of substance	f	a	d	α	β
$CH_3COCH{=}CHN(CH_3)_2$	0,008474 0,009021 0,010650 0,012918	2,5800 2,6338 2,6579 2,7418	0,87572 0,87582 0,87000 0,87636	16,081	0,150
$CH_3CH_2CH_2COCH{=}CHN(CH_3)_2$	0,008704 0,008943 0,010180 0,010308	2,562 2,567 2,608 2,614	0,87570 0,87573 0,87584 0,87584	14,631	0,152
$(CH_3)_2CHCH_2COCH{=}CHN(CH_3)_2$	0,006757 0,007612 0,00770	2,4892 2,5181 2,5180	0,87522 — 0,87523	14,358	0,113
$CH_3COCH{=}CHN(C_2H_5)_2$	0,007139 0,010039 0,010244	2,7303 2,7385	0,87547 0,87595 0,87605	20,135	0,164
	0,007944 0,009358 0,011287	2,5781 2,6420 2,7111	0,87662 0,87709 0,87755	17,242	0,309

The conjugation of the carbonyl group with the C=C double bond has almost no effect on the value of the moment, as can be seen from the example of mesityl oxide, the moment of which is 2.8 D, i.e. approximately the same as the moment of acetone. Three N–C bonds give a total moment of not more than 0.9 D. Evidence has recently appeared which indicates that the urea molecule is flat [2], i.e., the C–N and N–H bonds are arranged as if sp^2-hybridization occurred as a result of the existence of a strong internally ionized state. It is possible that this occurs also in our case. If that is so, then the three bonds will be mutually inclined at 120° and their moments will neutralize each other. In any case, in addition to the moment of the carbonyl bond the compounds have a considerable supplementary polarity on account of the conjugation with nitrogen. This is in accord with their chemical behavior. They are unable to undergo the diene synthesis, probably owing to the weakening of the double bond character of the C=C bond. Moreover, the Grignard reaction does not occur at the carbonyl group. The dipole-moment results do not provide an unequivocal answer to the question of cis or trans structure owing to the nonfeasibility of calculating from the vector sum of individual bonds in this case.

The difference between the moments of the substances (III) and (IV) indicates a small effect due to the alkyl group attached to the carbonyl. The substantial equality of the moments of (IV) and (V) indicates that further increase in the complexity of the alkyl group no longer affects the moment. The moments of the substances (I), (II), and (III) differ somewhat from one another. It would appear that groups attached to nitrogen have greater effects on the moment than groups attached to the carbonyl. Finally, we must point out that the dipole-moment results are in accord with the results of an investigation of the absorption spectra of these compounds [3].

SUMMARY

The dipole moments of five unsaturated amino compounds were measured. All of the substances were found to have considerable polarity. The enhanced polarity of these compounds is in accord with their chemical behavior.

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*T.p = C.B Translation pagination.

CYANOETHYLATION OF TRICHLOROSILANE

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It has been shown in previous papers [1,2] that organosilicon alcohols, amines, and thiols readily add to acryonitrile when the functional groups are α or γ with respect to Si. Organosilicon compounds having the same functional groups on the silicon are cyanoethylated with great difficulty. In the present investigation we have succeeded in effecting the addition of trichlorosilane to acrylonitrile in presence of Raney nickel:

$$HSiCl_3 + CH_2 = CHCN \xrightarrow[\text{Raney nickel}]{} Cl_3SiCH_2CH_2CN.$$

This reaction is the first example of cyanoethylation at an Si–H bond. The yield of 3-(trichlorosily.)propionitrile was 12.2%, only a little lower than the yield obtained under the conditions of direct synthesis [3].

EXPERIMENTAL

Synthesis of $Cl_3SiCH_2CH_2CN$. A mixture of 80 g of freshly distilled trichlorosilane, 35 g of acrylonitrile, and 5 g of Raney nickel was prepared in an autoclave, which was then heated at 160-170° for four hours. The maximum pressure during the reaction did not exceed 20 atm. The autoclave was cooled, and the reaction product was filtered from catalyst and solid polymer. Three fractionations gave a fraction (14 g) boiling at 79-82° (10 mm); it solidified on standing to give crystals of m.p. 32-33°. The literature [3] gives b.p. 84-86° (10 mm) m.p. 33-34°.

Found %: Si 14.67; 15.05

$C_3H_4Cl_3SiN$. Calculated %: Si 14.85

Synthesis of $(CH_3)_2SiCH_2CH_2COCH_3$. A solution of 9 g of $Cl_3SiCH_2CH_2CN$ in 50 ml of absolute ether was added over a period of 15 minutes to a Grignard reagent prepared from 38 g of CH_3I. After the usual treatment a ketone having the following properties was isolated: b.p. 82-85° (65 mm); d_4^{20} 0.8339; n_D^{20} 1.4231. The same ketone prepared previously by Petrov, Sadykh-Zade, and Vdovin [3] from $Cl_3SiCH_2CH_2CN$ synthesized by the direct method had the following properties: b.p. 81.5-83° (64 mm), d_4^{20} 0.8325; n_D^{20} 1.4235. Sommer and Nelson indicate similar properties for this ketone: b.p. 84° (65 mm); d_4^{20} 0.8330; n_D^{20} 1.4228.

Under the above-described conditions, the cyanoethylation reaction went also when trichlorosilane was replaced by dichloromethylsilane, but we did not succeed in isolating pure $Cl_2(CH_3)SiCH_2CH_2CN$ by fractionation. Furthermore, we did not succeed in isolating this compound when Raney nickel was replaced by other catalysts (palladium on copper and platinum on charcoal).

SUMMARY

It was shown that 3-(trichlorosilyl)propionitrile can be synthesized by the addition of trichlorosilane to acrylonitrile in presence of Raney nickel.

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DESTRUCTIVE HYDROGENATION OF 2-METHYLTHIOPHENE WITH HYDROGEN AT HIGH PRESSURE

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One of us and Nikitenkov [1] has previously investigated the destructive hydrogenation of toluene in absence of catalysts at 455-490° with hydrogen under high pressure (up to 1350 atm). This process results in the formation of benzene and methane together with a small amount of high-boiling products, among which biphenyl and bitolyl were isolated and identified. The homogeneity of this reaction was shown both in the investigation cited [1] and also in the earlier investigation of Nemtsov and Levin [2]. At the highest pressures used (1100 and 1350 atm) a little methylcyclohexane was also detected among the reaction products, the formation of this substance being probably associated with the catalytic effect of the autoclave walls (stainless steel).

It was considered to be of interest to compare the behavior of toluene under the conditions of destructive hydrogenation in absence of catalysts with that of 2-methylthiophene. Moldavsky in collaboration with Prokopchuk [3] and Kumari [4] has investigated the destructive hydrogenation of thiophene in absence of catalyst at 230-450° in an autoclave, the initial hydrogen pressures ranging up to 80 atm. Apart from hydrogen sulfide, these authors established the presence of tetrahydrothiophene among the reaction products, and they suggested that the autoclave walls might have a catalytic effect. Fricke and Spilker [5] had previously investigated the noncatalytic hydrogenation of thionaphthene at 425-438° under working pressures of 110-160 atm. Among the reaction products they isolated and identified benzene, toluene, ethylbenzene, 2-ethylthiophene, 2,3-dihydrothionaphthene, and anthracene. There are no data in the literature on the noncatalytic destructive hydrogenation of alkylthiophenes.

The results obtained in the present investigation show that there are substantial differences between 2-methylthiophene and toluene with respect to the course of the process of destructive hydrogenation under high pressures of hydrogen.

EXPERIMENTAL

The 2-methylthiophene used in our experiments had the following constants: b.p. 111.5° and n_D^{20} 1.5203 (the literature [6] gives b.p. 112.5° and n_D^{20} 1.5203). The experiments were carried out in accordance with the procedure already described [1] in a stainless steel autoclave having a capacity, including that of the manometer, of about 100 ml. The initial hydrogen pressure was 500 atm. Below, we give the results of two experiments at 400°.

Experiment 1. Load: 20.00 g of 2-methylthiophene. Duration of experiment at working temperature: 4 hours. Working pressure: 1070-850 atm. Residual pressure: 370 atm. When the autoclave was unloaded, the gaseous products were passed through 20% NaOH solution in order to absorb hydrogen sulfide, the amount of sodium sulfide formed being determined iodometrically. The gas was found to contain 2.02 g of sulfur, i.e. 31% of the amount in the original 2-methylthiophene. No appreciable amount of hydrocarbons could be detected among the gaseous products after removal of hydrogen sulfide.

The colorless liquid unloaded from the autoclave (13.60 g*; n_D^{20} 1.4962) was then subjected to chromatographic separation on a silica-gel column. The following fractions were obtained:

*The unloading losses were generally about 2 g, but in the experiment described they were higher than this.

Fraction I,	1.50 g;	n_D^{20} 1.3793
Fraction II,	3.20 g;	n_D^{20} 1.5058
Fraction III,	4.25 g;	n_D^{20} 1.5113
Fraction IV	2.60 g;	n_D^{20} 1.4895

It was later found that Fraction I owed its low refractive index to the presence of pentane. In Fractions II and III neither thiophene nor tetrahydrothiophene could be found by fractional distillation. Fraction IV was again passed through silica gel, and 1.46 g of a substance having n_D^{20} 1.4872 was isolated. This fraction was then distilled twice from a Wurtz flask, and a fraction boiling at 126-128° was collected and found to have n_D^{20} 1.4878. It was found to be tetrahydro-2-methylthiophene, for which the literature [7] gives b.p. 131.5° (756 mm), 132.5° (750 mm); n_D^{20} 1.4922; 1.4886.

Found %: C 58.88; 58.62; H 9.92; 9.92; S 31.20; 31.16
$C_5H_{10}S$. Calculated %: C 58.83; H 9.80; S 31.37

Experiment 2. Load: 51.7 g of 2-methylthiophene. Time at working temperature: 3 hours 30 minutes. Working pressure: 1000-650 atm. Residual pressure: 210 atm. The gas was found to contain 5.64 g of sulfur, i.e. 33.5% of the amount in the original 2-methylthiophene. The 43.6 g of colorless liquid unloaded from the autoclave was fractionated through a 17-plate column having a glass packing. The following fractions were collected:

Fraction I, B.p. 31-42°;	1.72 g;	n_D^{20} 1.3638
Fraction II, B.p. 42-79°;	1.24 g;	n_D^{20} 1.4112
Fraction III, B.p. 79-88°;	0.76 g;	n_D^{20} 1.4590
Fraction IV, B.p. 88-111°;	2.76 g;	n_D^{20} 1.5032
Fraction V, B.p. 111-112°;	15.12 g;	n_D^{20} 1.5173
Fraction VI, B.p. 112-114°;	6.74 g;	n_D^{20} 1.5183
Fraction VII, B.p. 114-125°;	1.06 g;	n_D^{20} 1.5044
Fraction VIII, B.p. 125-136°;	1.08 g;	n_D^{20} 1.4945
Fraction IX, B.p. 136-155°;	1.42 g;	n_D^{20} 1.4919
Fraction X, B.p. 155-170°;	1.87 g;	n_D^{20} 1.4888
Residue	7.50 g.	

Fractions I, II, III, VII, and VIII were then chromatographed. Fraction I yielded pentane, n_D^{20} 1.3580 (the literature [8] gives n_D^{20} 1.3575).

Found %: C 83.16; H 16.89
C_6H_{12}. Calculated %: C 83.33; H 16.67

Fractions V and VI consisted mainly of uncharged 2-methylthiophene, as was shown by a further fractional distillation.

Our attempts to detect and isolate thiophene (b.p. 84.1°) from Fraction III and tetrahydrothiophene (b.p. 121.2°) from Fraction VII were not successful. The non-formation of the latter compound is probably due to the lower partial pressure of hydrogen in Experiment 2.

The residue remaining after the fractional distillation of the reaction products was vacuum fractionated. The following fractions were obtained:

Fraction XI, b.p. 95-96° (20 mm); M 162; C 72.71%; 72.41%; H 9.38%; 9.33%; S 17.81%; 17.89%.
Fraction XII, b.p. 116-117° (20 mm); M 169; C 73.40%; 73.56%; H 8.73%; 8.61%; S 17.73%.
Fraction XIII, b.p. 144-148° (20 mm); C 71.28%; 71.24%; H 7.51%; 7.49%; S 21.43%.

These data on the composition of the high-boiling reaction products and their molecular weights enables us to infer that they contain a mixture of compounds having one sulfur atom formed by the addition of hydrocarbon radicals containing five carbon atoms to 2-methylthiophene (possibly partially hydrogenated) or to the radical formed by the opening of its ring. In fact, compounds having the empirical formulas $C_{10}H_{18}S$ and $C_{10}H_{16}S$ should contain respectively, 71.5% and 73.2% of hydrogen and 9.5% and 7.3% of sulfur (molecular weights 185 and 184 respectively), which are fairly close to the analytical results for Fractions XI-XIII.

SUMMARY

1. Our results indicate that, under the conditions studied, there is a very great difference between the processes occurring in the destructive hydrogenation of toluene and of 2-methylthiophene. We were unable to detect thiophene, tetrahydrothiophene, or methane among the reaction products, and so were unable to establish the occurrence of the dealkylation of 2-methylthiophene. On the other hand, dealkylation is an essential feature of the destructive hydrogenation of toluene.

2. The destructive hydrogenation of 2-methylthiophene occurs at lower temperatures, i.e. more rapidly, than the destructive hydrogenation of toluene.

3. The pentane and tetrahydro-2-methylthiophene that we have isolated from products of the destructive hydrogenation of 2-methylthiophene form only an insignificant part of the 2-methylthiophene that reacted. Unlike toluene, which gives practically only benzene and methane when subjected to destructive hydrogenation, 2-methylthiophene gives a mixture of various products.

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CURRENT EVENTS

CONFERENCE ON ELECTROCHEMISTRY AT THE POLISH ACADEMY OF SCIENCES

A conference on electrochemistry was held in the capital of the Polish People's Republic - Warsaw - on November 15-19, 1955. On the invitation of the Polish Academy of Sciences delegates from the Soviet Union and the People's Democracies (Czechoslovakia, Hungary, and the German Democratic Republic) took part in the work of the conference.

About forty papers were presented on various aspects of electrochemistry. Particular attention was paid to the role of the interfacial potential between phases in flotation and chromatographic processes, to the absorption of cathodic hydrogen by metals and its effect on mechanical and magnetic properties, to the theory of solutions, and to electrothermodiffusion.

At the first session Prof. M. Smialowski read a long paper entitled "Investigation of Electrochemistry in Poland, Past and Present". In Poland, work on electrochemistry began to develop shortly after the First World War. One of the centers of electrochemical research was the laboratory at the Jagiello University (Krakow), which in 1920 was directed by Prof. Bohdan Szyszkowski (1873-1931). In spite of the fact that Szyszkowski began his scientific work in the laboratory of the great organic chemist Reformatsky at Kiev, from the very beginning his work was essentially electrochemical. He worked on the relationship between the dissociation of organic acids and their molecular structures, and he later devoted his activities to the establishment of the laws of dissociation in weak electrolytes. Work in a similar direction was carried out by Marjan Hlasko (1921-1939) in Vilna University. Using a very accurate method of measurement, Hlasko made a systematic study of the conductivity and dissociation of various substances in aqueous and nonaqueous solutions. The speaker then discussed the work of Prof. Kazimerza Jablczynski of Warsaw University, who studied the theory of electrolytes, the kinetics of electrode processes, etching phenomena at electrodes, etc.

Prof. Smialowski discussed also the work of the eminent Polish scientist Prof. Smoluchowski, whose work on electrokinetic phenomena has been a stimulus for further investigators in this direction (that of G. Lyaksa in Warsaw, M.S. Glixelli and Prof. A. Galecki in Poznan, and particularly Prof. Kamiensky in Krakow). In treating polarography and polarographic methods of analysis, the speaker discussed the work of Wiktor Kemula, who began his scientific career in 1935 at Lvov University, but has recently worked in the Department of Inorganic Chemistry of Warsaw University.

Passing to a general appraisal of the development of electrochemistry in "old" Poland, Prof. Smialowski pointed out that a regrettable shortcoming was the absence of any close relationship between the subjects investigated and the needs of industry. The speaker stated that "the lines of work in our research institutes almost always followed - not always very successfully - those of West European research institutes, particularly German". Prof. Smialowski considered that the reasons for this lay in the lack of interest shown by investigators in industrial problems owing to the fact that the greater part of industry was in the hands of foreign capitalists, who not only did not submit any of their problems to the research institutes, but also refused to allow investigations to be carried out in the laboratories of the industrial concerns. The speaker cited examples showing how the American capitalists who owned the Polish zinc industry tried to prevent research from being carried out. He also gave interesting facts showing how foreign capitalists retarded the development of the electrochemical industry in Poland.

For example, American industrialists proposed to the Polish government that they should build a power station on the condition that they should receive the sum of 80 grosz per kw-hr, in spite of the fact that the cost of electricity at the power stations in Upper Silesia was 1.9 grosz per kw-hr.

In his concluding remarks Prof. Smialowski stated that after the Second WorldWar the electrochemical industry made extremely rapid progress in the Polish People's Republic, both quantitatively and qualitatively. Thanks to close cooperation with the Soviet Union and the People's Democracies, all the necessary conditions had now been

created for the rapid advancement of science in Poland.

At the first session, following Prof. Smialowski's address, a review paper was read by B.N. Kobanov (Moscow) on the effect of the specific adsorption of anions on the rate and mechanism of electrochemical processes. A distinction was drawn between the simple phenomenon of the establishment of an adsorption potential when ions are adsorbed at the surface of a dielectric and the complex phenomenon of the specific adsorption of ions at the interface between metal and electrolyte solution accompanied by the exchange of potential-determining ions between the phases. It was shown that, at metal and metal-like (oxide) electrodes, the specific adsorption of anions often leads to great changes in the rates of electrochemical processes, this being associated with change in the electrical structure of the electrode surface.

Papers were read also by B. Baranowski and his coworkers on the theory of diffusion and methods of measuring diffusion. In his paper, B.Baranowski, using Onsager's work, examined the thermodynamic theory of diffusion as applied to liquid alloys. The paper of J. Demichowicz and B. Baranowski was concerned with the electrothermodiffusion method of measuring the transfer of particles in aqueous electrolyte solutions, and it was shown that this method was to be preferred to the thermogravitational method.

M. Samowski and B. Baranowski presented a paper on the anomalous vapor pressure observed in certain three-component aqueous and nonaqueous solutions: in these systems the vapor pressure is considerably greater in concentrated solutions than in less concentrated solutions. Samowski and Baranowski referred to this anomalous behavior as "antiRaoultian". The authors consider that this anomaly is due to the formation of double salts or the interaction of ions with solvent molecules with formation of solvates of variable composition.

In a paper entitled "The Role of Hydrogen in the Electrodeposition of Metals" K.M. Gorbunova (Moscow) gave an exposition of the material that has led to the establishment of a relationship between the mechanical, magnetic, and optical properties of deposits, their structures, and their hydrogen contents. On the basis of a generalization of a large amount of experimental material, the speaker showed that it was necessary to distinguish a special group of deposits - an indistinctly crystalline type, which includes brilliant chromium, nickel, copper, and other deposits of practical importance. The mechanism of the formation of such deposits differs in principle from the mechanism of electrocrystallization, which is associated with periodic layer formation on the crystal faces. The absorption of hydrogen is regarded not as the cause of the strained state of the deposits, but as a consequence of the dislocation of the metal lattice owing to the incorporation of surface-active substances, including hydroxides forming at the cathode.

In his paper A.T. Vagramyan (Moscow) pointed out the part played by the nonuniformity of the cathode surface in the electrodeposition of metals; when account is taken of the presence of active sites on the electrode, it is possible to solve some problems of practical and theoretical importance.

Bogdan Kamienski (Krakow) read a paper on the role of the electrical potential arising at the phase interface in processes of adsorption, flotation, and chromatography. Kamienski's paper was supplemented by papers presented by his students. Thus, B. Waligora described the essential features of the potentiometric method of chromatography, which consists in the measurement of the variation of the potential of a micro-element as the effluent from an adsorbent column passes over it. The speaker gave various examples showing how the method made it possible to separate mixtures of pyridine derivatives, fatty acids, etc.

I. Kulavin noted still another characteristic property of the micro-electrode, namely its high sensitivity to gases. He showed that by making use of this fact it was possible to determine traces of certain gases and vapors (iodine, bromine, chlorine, hydrogen sulfide, and others) in air and in nitrogen. For example, the micro-electrode is sensitive to 0.00007% of chlorine in air.

A. Pomianowski gave an address on electrical phenomena accompanying flotation processes. He showed that the effect of the flotation reagent (xanthate) on the electrode potential is greater in acid solutions than in alkaline. A study of the effect of a "suppressor" (potassium dichromate) on the potential of the mineral, makes it possible to establish the optimum ratio between the concentrations of flotation reagent and "suppressor".

W. Kemula's paper was devoted to the chromatopolarographic method and its application to the investigation of inorganic and organic compounds. Kemula showed that this combined method opens up new possibilities for the investigation of the most varied types of chemical compounds.

S. Lingiel (Budapest) read a paper entitled "Investigation of the Distribution of Molecules and Aggregates in Electrolyte Solutions and Other Two-Component Solutions". Prof. Lani (Budapest) reported the results of work on phosphating carried out in his laboratory.

The conference listened also to accounts of the work of the M. Smialowski school (Warsaw) on the overvoltage of hydrogen, the mechanism of the cathodic absorption of hydrogen by metals, and the effect of hydrogen absorption on the mechanical properties of metals. A. Krupkowski and M. Smialowski's paper presented experimental results on the deformation of an iron wire resulting from the absorption of hydrogen during electrolysis. M. Smialowski presented a paper describing the effect of change in polarization conditions on the brittleness produced in iron and nickel under the influence of the absorbed hydrogen. It was observed, in particular, that in presence of arsenic the brittleness of iron polarized in sulfuric acid was considerably greater than in the absence of arsenic; in presence of dibenzyl sulfoxide, however, the brittleness was less. It was shown that the effect of cathodic hydrogen on the mechanical properties of nickel was considerably less than its effect on iron, this difference being explicable by the difference in the catalytic properties of these metals for the recombination of hydrogen atoms to form molecules. In J. Forist and M. Smialowski's paper it was shown that the brittleness is due to the accumulation of hydrogen at defects in the metal structure, i.e. at inclusions of oxides, sulfides, etc.

W. Palczewska read a paper on the effect of certain organic substances and catalytic poisons on the overvoltage of hydrogen at iron and nickel cathodes. G. Jarmolovicz analyzed the effect of catalytic poisons on the overvoltage of hydrogen and the yields obtained in the reduction of nitrobenzene, tungstic acid, and other substances. L. Kozlowski (Kliwice) gave a very thorough discussion of the theme "The Effect of Hydrogen Formed at the Cathode on the Magnetic Properties of Mild Steel". J. Koryta (Prague) read an interesting paper on electrode reactions investigated by the polarographic method, and J. Kuta (Prague) discussed the mechanism of the separation of hydrogen at mercury electrodes.

S. Minc (Warsaw) gave an interesting review paper on the work carried out under his supervision. The main theme of the paper was the investigation by optical methods (Raman and absorption spectra, refractometry) of the relationship between the structure of electrolytes and the nature of the medium. Lech Stolarczik discussed the use of absorption spectra in the study of the structures of complex compounds.

On the basis of the results of investigations on the structure of nitric acid, carried out with the aid of Raman spectra, Z. Kecki concluded, in his paper, that the nitration of aromatic compounds is brought about not only by the ion, but also by the undissociated molecule of nitric acid. He considers also that the process proceeds the more readily, the greater the polarization of the $HO-NO_2$ bond in the given medium and the lower the energy required for the removal of a proton from the aromatic compound. W. Libus read a paper on the solvation of copper and cobalt ions in water and in organic solvents, this being investigated with the aid of absorption spectra. G. Angerstein (Warsaw) described his work on the mechanism of the cathodic atomization of lead; he showed that alkali metals formed an alloy with lead at the surface of the lead cathode, and this alloy was the source of the atomization.

In conclusion we must mention that the papers received very thorough discussion, and we must emphasize particularly the active part taken by the younger people in this discussion. The work of the conference demonstrated the wide range covered by the research into theoretical and applied electrochemistry now being carried out in the Polish People's Republic. Such conferences, in which scientists of different countries take part, are extremely useful in promoting the extensive exchange of experience between scientists, and they will undoubtedly further the fruitful development of science.

Prof. A.T. Vagramyan

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IN FURTHERANCE OF CONTINUING PROGRESS IN THE SCIENCE OF CHEMISTRY

The Twentieth Congress of the Communist Party of the Soviet Union has now completed its work. The resolutions passed at the Congress are of great historical importance: they lay down the program to be followed in the struggle for the establishment of a communist society in our country, for the consolidation of peace throughout the world, and for the triumph of the ideas of Marxism-Leninism.

The Congress heard and discussed the Report of the Central Committee of the Communist Party of the Soviet Union, which was read by the First Secretary of the Central Committee, Comrade N. S. Khrushchev. The Report of the Central Revisory Committee, which was read by P. G. Moskatov, was also discussed.

In approving the Report of the Central Committee of the Communist Party of the Soviet Union, the Twentieth Congress passed a resolution which expresses the collective views and wishes of the Party and which constitutes an extremely important program of action.

The Congress heard and discussed the Report of the Chairman of the Soviet of Ministers of the USSR, Comrade N. A. Bulganin, concerning the directives in the Sixth Five-year Plan for the development of the national economy of the USSR in 1956-60. The Congress ratified these directives. The Congress decided to make some modifications in the party statutes. It resolved also that, for the next party congress, a party program should be prepared which would reflect the basic principles of Marxist-Leninist theory, as creatively developed on the basis of the historical experience of our party and the experience also of the fraternal parties of the socialist countries and of all the other international communist and working-class movements. Consideration was given also to the long-term plan that has been prepared for the building of communism and the development of the economic structure and culture of the Soviet Union.

The Congress elected the central executive bodies of the Party.

In the Report of the Central Committee the Twentieth Congress of the Communist Party was presented with a close analysis of the present international situation. In this report, Comrade N. S. Khrushchev made a scientific summing up of achievements in national economy, state organization, and culture in the Soviet Union. In the years between the Nineteenth and Twentieth Party Congresses, the Lenin Central Committee has shown notable perspicacity in the assessment of the internal and external situations. N. S. Khrushchev's report reflects a creative fighting spirit applied to the grandiose tasks of building up a communist society.

The scientifically developed Marxist-Leninist theories of the peaceful coexistence of two systems, of the possibility of avoiding war in the present period, of the forms of transition to socialism in different countries, and of the attitude to be taken to social-democratic parties are of great fundamental importance. These important and theoretically bold conclusions, which are associated with the laws of social evolution and their application under present-day conditions, acquire the character of a program and are of great practical importance in determining the correct policy to be adopted in the next stages of building up a communist society.

In the resolution on N. S. Khrushchev's report the Congress noted with great satisfaction the further consolidation of the internal position of the Soviet Union. The resolution states that, as a result of the work of the Central Committee in consistently marking out the general party line, there has been a considerable rise in production in all branches of industry and agriculture, and a great improvement in the material well-being and cultural level of the people. The true basis of all socialist economics was, and still is, the preferential development of heavy industry. The determining factor in the further growth of our industry is continual technical progress. The Congress pointed out the special importance of the incorporation of the discoveries of science into the national economy. In an atmosphere of great political enthusiasm, the Congress carried a unanimous resolution registering its full approval of the line of policy and practical activities of the Central Committee of the Communist Party of the Soviet Union, and also of the practical propositions and conclusions contained in the report.

In Comrade N. A. Bulganin's report on the "Directives of the Twentieth Congress of the Communist Party of the Soviet Union relating to the Sixth Five-year Plan" and in the resolutions taken on this report, a picture was

given of the grand prospects before us in the further growth of our state. In the approved directives of the Twentieth Congress for the Sixth Five-year plan for the development of the national economy of the USSR in 1956-60, we are set tasks which are of the highest importance and require an enormous increase in the productive capacity of our country.

The directives state: "The performance of the principal tasks set by the Sixth Five-year Plan for the development of the national economy of the USSR demands, as a basis, the preferential development of heavy industry, continual technical progress, and rise in the productivity of labor so that there may be further rapid advances in all branches of the national economy and a rapid rise in agricultural production, the result being a considerable improvement in the material well-being and cultural level of the Soviet people." The fulfillment of this plan for the development of the national economy of the USSR in 1956-60 will be an important step in the solution of the main economic problem of the USSR — to draw level with and pass the most advanced capitalist countries in the production of the goods required to meet the needs of the people.

Grandiose, exacting tasks lie before Soviet chemists. It is sufficient to state that the volume of production set for the most important industrial products in 1960 — the last year of the Sixth Five-year Plan — is as follows: petroleum 135,000,000 tons (191% of the volume of production in 1955), gas 40 billions cu·m (almost four times as high as in 1955), mineral fertilizers 19,600,000 tons (twice as high as in 1955), and caustic soda 1,000,000 tons (177% of the volume of production in 1955).

One of the most important problems of the chemical and petroleum industries will be to bring about a sharp increase in the use of natural gases and petroleum products in the manufacture of synthetic alcohols, resins, and rubbers, high-quality soap substitutes, and synthetic materials for machine construction, radio technology, and other branches of the national economy.

The directives of the Twentieth Congress of the Communist Party of the Soviet Union with respect to the Sixth Five-year Plan point out the necessity for the development of science in all possible ways and the extension of theoretical investigations in all branches of knowledge. The part played by scientific institutes in the furtherance of technical progress and the organization of production must be extended. Much work has to be done by the scientific research institutes in bringing their activities closer to the actual needs of the national economy. In designing and planning organizations it is essential that the maximum use should be made of the achievements of Soviet and foreign science and technology. The efforts of scientists must be concentrated as much as possible on scientific problems of importance for the national economy. It is essential that the research institutes should be better provided with modern scientific equipment and that more of the scientists at the higher-education establishments should be drawn into scientific research.

Soviet chemists have great tasks before them in the development of work in various fields of great importance. A few of these tasks are outlined below.

Physical and Theoretical Chemistry. The study of the relationship between the structure and reactivity of compounds must be intensified. In this study questions of the mutual effects of atoms in molecules and the nature of the elementary chemical act in its relation to the structures of the reacting species (molecules, ions, radicals) and to the nature of the medium will be of great importance. In the first place elementary acts occurring in liquid-phase and heterogeneous reactions must be studied. It is necessary to make a quantitative study of the mechanism, kinetics, and stereochemistry of reactions in gaseous, liquid, and solid phases. In reactions of practical importance (cracking, oxidation-reduction reactions in the liquid phase, oxidation of organic substances, etc.) it is important to determine the identity and chemical properties of the active intermediate substances and to study the elementary stages in which they take part. Work on the solution of these problems in the theory of the chemical process must form the basis for the devising of effective methods of controlling the directions of chemical reactions.

Photochemistry. Much attention should be given to the effects of radiation on matter over a wide range of frequencies (from the infrared to the ultraviolet) — in particular, in their relation to the problem of photosynthesis. Apart from development in the biological direction, it is important to develop also the physicochemical side of photosynthesis. The field of photoluminescence, particularly the search for new luminophores, borders closely on this problem.

Theory of Catalysis and the Scientific Principles of the Selection of Catalysts. The development of this field is of great importance. The main tasks will consist in the determination of the relationship between the catalytic properties of substances and their compositions and structures, and also in the study of the kinetics and mechanisms

of catalytic processes used in various branches of industry, especially the chemical and petroleum-refining industries. There can be no disputing of the fact that investigations on catalysis must be carried out on the reactions of greatest practical importance.

Chemical Thermodynamics. Investigation must develop mainly in the direction of the study of the thermodynamic properties of chemical compounds. No less importance must be attached to work on the theory of aqueous and nonaqueous solutions, the main attention being turned to the study of nonaqueous solutions (metallic solutions, salt and oxide melts), which are of great importance for metallurgy.

Electrochemistry. Attention should be directed mainly to the theory of electrode processes (which forms the basis for work on new chemical sources of current), to methods of electrolysis, to the preparation of new types of deposits, and to the electrosynthesis of various organic compounds. These theoretical and experimental investigations will be important also for the solution of other chemical problems.

Inorganic Chemistry. Attention must be devoted mainly to the development of the chemistry of the individual elements, particularly the rare elements. The most important problems here are the discovery of methods of obtaining increased yields in the extraction of these elements and the preparation of the elements in a highly pure state. Special technical significance is attached to problems associated with the extraction of germanium, titanium, and zirconium, since in the near future the scale upon which these metals are used will be greatly extended.

In the Sixth Five-year Plan it is essential that there should be extensive study of the inorganic compounds of boron, fluorine, and silicon. It is essential to extend and intensify work on the synthesis and properties of metal peroxides, ozone derivatives, etc. Of no less importance is the task of intensifying the investigation of new salt-bearing deposits and developing the scientific principles underlying their utilization, particularly in districts in which rich salt deposits have recently been discovered (Belorussian SSR, Kazakh SSR, Kirgiz SSR, and some of the south-western districts of the USSR).

Analytical Chemistry. In this field, which is of special importance at the present time, the main task consists in the development of rapid, exact, automatic methods of analysis. Of no less importance will be accurate methods for the determination of small amounts, sometimes the merest traces, of impurity. It is essential to concentrate attention on the devising of new, and the perfection of existing, physicochemical methods of analysis (mass spectroscopy, radioactivation analysis, multichannel photoelectric spectroscopy, the use of ultrasonics and isotopes, etc.).

Apart from the development of analytical methods, it is necessary also to develop the theory of analytical chemistry, in particular the chemistry of substances in solution. Studies must be made of the processes occurring in the separation of substances by the methods of chromatography, extraction, fractional distillation, etc.

Geochemistry. Investigators are faced by a series of problems relating to the laws determining the distribution, transfer, and concentration of elements in different geological processes. The solution of these problems will greatly facilitate the scientific, geochemical direction of the search for new ore deposits.

The main directions of scientific research in geochemistry during 1956-60 must lie both in the development of physical and physicochemical methods for the investigation of mineral raw material and also in the extension of investigations on the geochemistry of isotopes with the object of determining the absolute age and origin of useful ore deposits.

Organic Chemistry. One of the most important theoretical problems of organic chemistry is the establishment of the relationship between structure and reactivity. In the further development of organic chemistry important parts must be played by physical methods, the methods of chemical kinetics, optical methods (in various frequency regions – from the infrared to the far ultraviolet), X-ray, electron, and neutron diffraction, mass spectroscopy, radiospectroscopy, methods of studying magnetic and electrical properties, etc. The application of stable and radioactive isotopes must be substantially developed. The solution of various theoretical problems and problems of computation demands a great intensification of studies in quantum chemistry.

The development of organic chemistry should proceed in the following main directions:

The development of synthetic methods and routes of synthesis for the intermediate and ultimate products of chemical industry (plastics, synthetic fibers, rubbers, solvents, toxic chemicals, growth-promoting substances,

synthetic detergents, new fuels, etc.). The raw materials for these syntheses must be petroleum, cracking gases, and industrial and natural gases. The main method of synthesis must be the catalytic method.

The synthesis and wide application in new technical uses of organic compounds containing silicon, fluorine, nitrogen, phosphorus, aluminum, boron, and other elements.

The investigation of new physiologically active compounds and proteins isolated from animals and plants, and the synthesis of these compounds or their analogs with the object of utilizing them in various fields of the national economy.

The development of methods of synthesis of macromolecular compounds, and the establishment of the relationship between the properties of these compounds and their structures.

In conclusion, it must be emphasized that chemistry must be developed from all sides. This is required by the directives of the Twentieth Congress of the Communist Party of the Soviet Union relating to the Sixth Five-year Plan. Only then can we expect to obtain a "point of growth". It is essential also to develop the theory of chemical structure and the chemical kinetics of gas and liquid reactions, quantum chemistry, and chemistry of rare elements, radiochemistry, the chemistry of natural compounds, particularly proteins, and other fields. The great variety and wide applicability of various physical and physicochemical methods of investigation will assist greatly in the further progress of chemistry.

Great tasks are set by the directives of the Twentieth Congress of the Communist Party of the Soviet Union with respect to the Sixth Five-year Plan for the development of the national economy of the USSR in 1956-60. Our scientists, working creatively hand in hand with the Soviet people, will advance science still further in the cause of the welfare and prosperity of our Fatherland.

Armed with the great, vital teaching of Marxism-Leninism, and closely consolidated around the Lenin Central Committee, the Communist Party boldly guides our country forward toward the complete triumph of communism.

THERMODYNAMICAL INVESTIGATIONS OF WETTING PHENOMENA

A. V. Dumansky

(Paper read at a General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, October 28, 1955)

1. Colloidal systems have come to be regarded — particularly after the investigations of Wolfgang Ostwald and Freundlich — as polyphase systems containing clearly defined interfaces. The theory of surface phenomena has therefore acquired great importance for colloid science. Lyophilic character in dispersed systems has been investigated from the point of view of surface energy, numerous detailed studies having been carried out since the beginning of the century. Knowing the specific surface and assuming the presence of a unimolecular layer, one may readily calculate the amount of liquid adsorbed per unit area of the surface, a quantity that can be used to characterise the lyophilic character of the system.

Important investigations on surface phenomena have been carried out in the USSR, particularly in the laboratories of B. V. Ilyin, M. M. Dubinin, and A. V. Kiselev. Detailed reviews of work carried out here and abroad can be found in the books of Kiselev [1], Adam [2], Rideal [3], Dubinin, Ilyin, and others.

All these discussions of lyophilic character can be applied more or less rigorously only to systems in which the dispersed phase forms a strictly defined interface with the dispersion medium. Most lyophilic colloids (colloidal systems based on macromolecular compounds) do not possess clearly defined interfaces associated with their micelles, molecular aggregates, and individual molecules, and it is sometimes doubtful whether they can be said to possess any surface intermicellar energy. From these considerations it will be seen that the study of the lyophilic character of colloidal systems on the basis of the concept of surface energy is not always possible, except in the case of suspensoids — although, even in this case, it is not always possible to identify surface tension and free surface energy [4].

Two quantities — the heat of wetting of unit mass of colloid and the amount of medium (e.g. water) sorbed by this mass — are characteristic of all colloidal systems and are more or less readily measured directly. These two quantities which are closely related to one another, are related also to the surface energy of dispersoids and to the energy of interaction between macromolecules and molecules of the liquid medium. On the basis of these two quantities we may make a direct study of the lyophilic properties of colloidal systems of all types. Owing to this interrelationship, Rebinder's proposal — that the coefficient q_1/q_0 (q_1 is the heat of wetting the dry object with water and q_0 is the heat of wetting with hydrocarbon) be taken as a measure of hydrophilic character — becomes applicable to all systems.

In our laboratory at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR (coworkers: S. F. Bykov, R. V. Voitsekhovsky, P. A. Demchenko, L. G. Demchenko, I. A. Dumansky, O. D. Kurilenko, Ya. F. Mezheny, R. V. Mikhalyuk, E. F. Nekryach, F. D. Ovcharenko, and V. I. Solnyshkin) detailed investigations have been made into the relationship between the heat of wetting and the amount of medium sorbed (generally water). Heats of wetting were determined on the dry colloids in an adiabatic calorimeter. Owing to the high magnitude of the heat change and to advantages gained by the use of an adiabatic calorimeter, the accuracy attained was fairly high. The amount of bound water can be determined in various ways [5-8], and the values obtained agree fairly well. For example, the amount of water bound by 100 g of dry starch, as determined cryoscopically, calorimetrically, by indicator methods, from the dielectric constant, from density determinations, and by other methods, is found to have the average value A = 33.4 g, the range of variation being 32-35 g.

2. In the final analysis, the heating of wetting is the result of interaction between molecules of the wetting liquid and molecules of the body being wetted. The nature of the forces linking molecules together varies and is dependent on the kinds of molecules that are interacting. Setting aside the forces of chemical interaction, we may mention that the interaction between molecules may result from orientation, induction, and dispersion effects. The

structures of the molecules determine which sort of interaction will predominate in any given case. Also, interaction between molecules may often result from hydrogen bonding. In such cases the hydrogen bond will be superimposed on the forms of interaction mentioned above. This fact is particularly important in the investigation of hydrophilic character.

Hydrogen bonding occurs in cellulose, starches, proteins, and other macromolecular compounds. This kind of bonding often predominates when water molecules interact with adsorbents and with molecules of macromolecular compounds in aqueous solutions.

3. Let us examine the case of the wetting of an insoluble adsorbent by water when the interaction between the molecules of the liquid and solid phases is due mainly to hydrogen bonding. The mechanism of wetting can be presented as follows. The molecules of liquid water $(H_2O)_n$ decompose into simple H_2O molecules with adsorption of heat ($-Q_d$ cal). Sorption of these on an unalterable sorbent then proceeds with evolution of heat ($+Q_w$ cal). When the process is carried out in a calorimeter we determine the quantity of heat

$$Q = Q_w - Q_d \qquad (1)$$

As a result of the process A grams of free liquid water becomes bound at the surface of the adsorbent. $Q/A = q$ is the heat of formation of 1 g of bound water. In the case of a highly polymeric adsorbent, the aggregates of which may dissociate into more simple ones on which sorption will occur, it is necessary also to take the heat of dissociation of the polymer aggregates, Q_k, into account, so that

$$Q = Q_w - Q_d - Q_k.$$

The magnitude of Q indicates that the heat of wetting is essentially the heat evolved in the passage of water from the free state to the bound state. This change can be regarded as a phase change, the new phase being characterized by its two-dimensional character – a film approximately one molecule in thickness. If in the wetting process A grams of water is bound by 100 g of dry substance and Q cal is evolved, then $100 \cdot Q/A$ is the heat evolved in the passage of 1 g of water into the bound condition. Investigations have shown that the heat of wetting various substances with water is constant when related to unit mass of bound liquid. For 1 g of bound water we may write $100 \cdot Q/A =$ = about 80 cal/g, or for 1 mole – about 1500 cal/g. The extent to which such constancy is observed [5] will be seen from Table 1.

TABLE 1

Substance	$100 \cdot Q/A$	Q	A	$\frac{1}{c} \Sigma \frac{\Delta q}{\Delta x}$
Potato starch	78	28.1	35.1	80
Sulfite cellulose	80	13.0	16.2	78.4
Agar	80	44.9	56	77.9
Gelatin (insol. fraction)	80	32.6	40.7	83.5
Silica gel	80	22.7	28.3	75.9
Soda soap (stearate)	80.5	4.5	5.6	80.0

TABLE 2

Kind of cellulose	A (per 100 g)	Q (cal/g)
Cotton	12.75	10.2
Sulfite	17.2	13.8
Nitric-acid	23.75	18.9
Sulfate	21.6	17.2

Rode [7], applying the data of various authors on the heats of wetting of dry soils and assuming that the lowest moisture regain A at which the differential heat of wetting is zero corresponds to bound water, calculated values of $100 \cdot Q/A$ and found that it had the same constant value of 80 cal/g. Moore's investigations (1953) confirmed the law that we had stated concerning the constancy of the amount of heat evolved when unit mass of bound water is absorbed, the cottons examined being various textile fibers [8]. In a study of the sorption coefficient of water, Andrianov [9] found that Q/A was very nearly constant.

The constant Q/A can be obtained graphically from the isotherm for integral heats of wetting Q as a function of the moisture regain of the adsorbent. Such isotherms were given by Rodewald [10] for starch. Many workers have determined isotherms of this sort in recent years. We have determined isotherms for starch, gelatin, silica gel, clays, etc., and some of the curves are shown in Fig. 1.

The integral curves can be used to construct curves for the differential heat of wetting as a function of the moisture regain of the adsorbent x (Fig. 2). The area bound by the curve and the axes of coordinates is equal to the integral heat of wetting of the dry adsorbent. Let us represent this area as a rectangle having one side equal to the

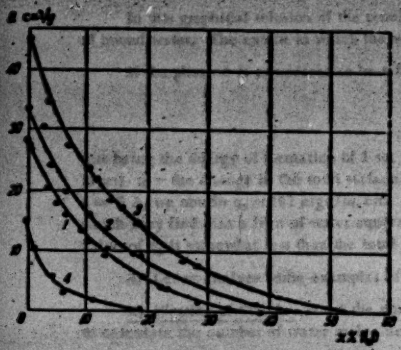

Fig. 1. Isotherms of integral heats of wetting: 1) potato starch; 2) gelatin; 3) agar; 4) sulfite cellulose.

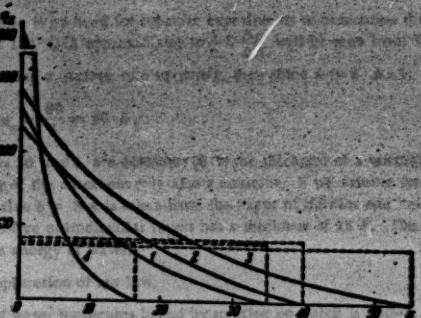

Fig. 2. Isotherms of differential heats of wetting: 1) potato starch; 2) gelatin; 3) agar; 4) sulfite cellulose.

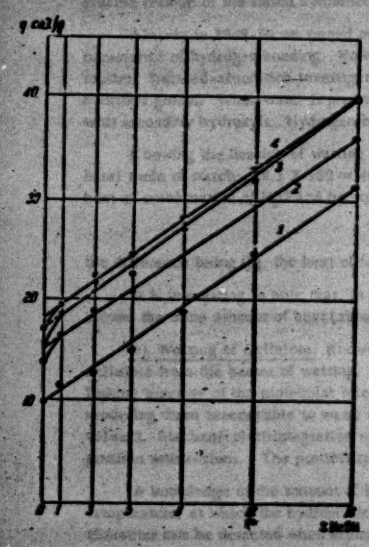

Fig. 3. Isotherms of the heats of interaction of cellulose with caustic soda solutions: 1) cotton; 2) sulfite cellulose; 3) nitric-acid cellulose; 4) sulfate cellulose.

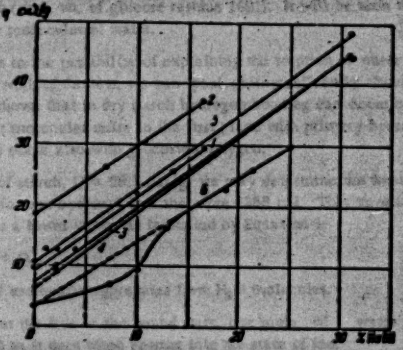

Fig. 4. Isotherms of the heats of interaction of cellulose with caustic soda solutions (data from the literature): 1) natural cotton (Morrison et al.); 2) the same after mercerization; 3) sulfite cellulose washed with alcohol (Voitsekhovsky et al.); 4 and 5) the the same (different kinds); 6) cotton cellulose (Barratt and Lowig).

least moisture regain c at which the differential heat of wetting q= 0. I.e. the amount of bound water A, so that the other side will be equal to the amount of heat evolved when 1 g of water is bound. A whole series of integral-heat curves was treated in this way, and it will be seen (Fig. 2) that the heights of the r-rectangles (in the ordinate direction) are substantially the same, i.e. Q/A is a constant (about 80 cal).

The curves we have discussed correspond to the equation Q= f(x), which Rodewald and later investigators did not succeed in solving. Mchryach suggested that, on the basis of the wetting isotherms, it should be possible to prove the equation Q/A = constant [11].

In this graphical solution of the problem, there is no need for separate experiments to determine the amount of bound water. The extent to which the value of $100 \cdot Q/A$ approximates to $\frac{\lambda}{c} \Sigma \frac{\Delta q}{\Delta x}$ will be seen from Table 1.

If the phase A is considered to be a film wetting a surface of S sq·cm/g, then since $A = S \cdot \delta \cdot 1$:

$$q_s = \frac{80}{S} = 80 \cdot \delta,$$

this being the energy of formation of 1 sq. cm. As 80 and δ are constants (δ is the thickness of a unimolecular layer), q_s – the change in the total surface energy of the adsorbent – is also a constant. If we assume the value $\delta = 3$ A, we obtain $q_s = 101$ ergs/sq. cm. The value $\delta = 3$ A is taken from the paper of Harkins and Jura [12], in which they find that a film of water equivalent to five unimolecular layers has a thickness of 15 A. The resulting value of q_s is somewhat less than the total surface energy of water.

4. Let us analyze some examples of the application of our law.

a) Wetting of Starch. When the number of water molecules bound by sorption on starch is known, it is easy to calculate the number of water molecules n combined with one glucose residue of the starch:

$$n = \frac{0.334}{18} \cdot 162 = 3.$$

[0.334 g of water (mol. wt. 18) per gram of starch (mol. wt. of glucose residue 162)]. It will be seen that each glucose residue of the starch combines with three molecules of water.

Already in 1949-50 we turned our attention to the possibility of explaining the sorption of water by starch by the occurrence of hydrogen bonding. Now, after the work of Samets, we can speak quite confidently about this matter. Infrared-absorption investigations have shown that in dry starch hydrogen bonding can occur between hydroxyl groups. When water is present the water molecules unite in the first place with primary hydroxyls, and then with secondary hydroxyls. Hydrogen bonding can occur also with glucosidic oxygen.

Knowing the heating of wetting one gram of starch, $Q = 28.1$ cal/g, we may determine the heat for one basal mole of starch: $28.1 \times 162 = 4698.1$ cal; for one hydroxyl it is therefore 1566 cal. This quantity is not the heat of combination of H_2O and hydroxyl, but has a lower value, as indicated by Equation 1:

$$Q < Q_w$$

the difference being Q_d, the heat of formation of molecular aggregates from H_2O molecules.

It is interesting to note that, in passing from the free to the bound state, one mole of water gives up almost the same amount of heat (about 1500 cal) as it does when passing into the state of ice.

b) Wetting of Cellulose. Knowing that $100 \cdot Q = 80 \cdot A$, we may determine the amount of bound water in cellulose from the heates of wetting. Calculation of n gives a value of less then 3 (2 or 1). It is clear that the linking together of the molecular micelles in the strong fibers results in the screening of some of the hydroxyls, rendering them inaccessible to water molecules. When the cellulose is ground, n increases, even attaining the value 3. Mechanical disintegration may lead to ring rupture, exposure of hydroxyls, and increase in the number of possible interactions. The possibility of ring rupture is referred to by Stepikheev [13] and also by Pauca [14].

A knowledge of the amount of bound water and the heat of wetting enables us to estimate the optimum drying temperature, at which the hydrophilic character is not affected. Experiment shows that no change in hydrophilic character can be detected when drying is carried out in a vacuum at 55-60°.

Lauer [15] determined the heats of wetting Q of various kinds of cellulose and their densities in water and in carbon tetrachloride. From these densities we have calculated the amount of water bound by sorption (from Voinukhovsky's equation [16]), and, knowing Q (Lauer), we have calculated the value of $100 \cdot Q/A$, which was found to be about 80. Satisfactory confirmation of our law was thus obtained.

The view that the water molecules combine at the hydroxyls is confirmed by the experiments of Hokagawa [17], who studied the heats of wetting acetylated polysaccharides (starch, glycogen, and inulin) with water and showed that they were considerably lower than those of the unsubstituted materials.

As can be seen from Table 2, different kinds of technical cellulose have different heats of wetting and therefore differ in the amount of bound water (hydrophilic character).

Data on heats of wetting provide an approach to the explanation of the mechanism of mercerization with caustic soda solutions of various concentrations applied to various kinds of cellulose [18]. Experiments have shown that the heat of wetting with such solutions is a linear function of the alkali concentration C. The results of these experiments are shown in Figures 3 and 4. Heats of wetting of various kinds of cellulose are plotted as ordinates, and alkali concentration as abscissae. The result is a series of almost parallel lines, curved only in the neighborhood of the axis of ordinates. This family of straight lines satisfies the following equation:

$$Q = q_0 + \frac{dQ}{dC} \cdot C; \quad Q = q_0 + C \cdot \tan \alpha,$$

(Q is the heat evolved in the process, q_0 is a constant for each kind, and α is the slope of the curves); tan α varies from 1.10 to 1.25.

The quantity Q is made up of two quantities: q_0, the heat of wetting by water (see Table 2), and the heat of reaction with caustic soda. The heat of wetting by water is determined by the accessibility of the hydroxyls to the reagent, i.e. the degree of degradation of the fiber, which is not the same for different kinds of cellulose. On the basis of these experiments we may arrange the kinds of cellulose in the following series: cotton < sulfite < nitric-acid < sulfate.

c) As a further example, let us examine the hydrophilic character of Capron (6-nylon), which has the formula:

$$HOOC(CH_2)_5 \cdot NH[CO(CH_2)_5 \cdot NH]_n \cdot CO(CH_2)_5 \cdot NH_2^0$$

According to Mikhailov and Skuratov [19] the heat of wetting is 6.3 cal/g for the unoriented fiber and 6.8 cal/g for the oriented fiber.

From the equation M/n = 18 X 80/Q we obtain M/n = 229 and 212, respectively, for the fibers. The monomer has a molecular weight of M = 113. We thus see that for each pair of monomer units there is one hydrogen bond associated with a water molecule, the remaining hydrogen bonds being concerned in cross-linking the molecules among themselves. On the basis of infrared absorption spectrum measurements, Shigorin, Mikhailov, and Makaryeva [20] have shown that inter- and intra-molecular hydrogen bonding may occur in this system.

d) Soaps – Their Lyophilic Character [21]. The heats of wetting sodium stearate and sodium palmitate with water were determined, and with the aid of our formula the number of water molecules combining with one molecule of soap was calculated. It was found that one water molecule becomes attached, and the "hydrates" can be assigned the following formulas:

$$CH_3(CH_2)_{16}-COO \cdots\cdots H_2O$$
$$\quad\quad\quad

$$Q = 0.065 \cdot n.$$

In the wetting of stearate, therefore, the heat evolved should be 0.065 X 18 = 1.17 cal, which is close to the experimental value of 1.16 cal; for palmitate we have 0.065 X 14 = 0.91 cal, and experiment gives 0.94 cal.

This rule is applicable to saturated soaps and saturated hydrocarbons. In unsaturated soaps, the zig-zag form of the chain and the mobility of the molecule at the double bond results in a screening of the units of the chain by one another, and the amount of heat evolved is reduced. The amount of heat evolved is therefore given by:

$$Q = \frac{0.065}{2} \cdot n.$$

Oleate again contains 18 carbon atoms in the chain, but, as it contains a double bond, according to the formula it can give only

$$Q = 9 \text{ X } 0.065 = 0.58 \text{ cal.}$$

The experimental value is 0.54 cal, i.e. close to the calculated value. Ricinoleate, which has carbons in its chain, has Q = 0.47 cal. Here, in addition to the screening referred to above, the OH group screens the neighboring CH_2 group. The general formula for the wetting of such soaps with a hydrocarbon can therefore be written:

$$0.065\,(n/2-1) = 0.065 \text{ X } 7 = 0.45 \text{ cal,}$$

i.e. a value very close to that found experimentally (0.47 cal). On the basis of these experiments, with respect to oleophilic character the soaps can be placed in the series:

Stearate > oleate > ricinoleate

1.16 0.54 0.47 cal

e) On the basis of the heats of wetting of soaps by hydrocarbons we may give the energetic mechanism of detergency [22].

In order that fatty (oily) spots may be washed from a fabric, it is necessary that the energy of the attachment of the fat (hydrocarbon) to the fabric (e.g. cellulose) be less than the energy of the binding of the fat to the soap. Wetting of cellulose with octane yields 0.37 cal, with paraffin oil 0.35 cal, and with sunflower oil 0.46 cal. The heat of wetting soap with oil is

$$Q = n \cdot 0.065 \text{ cal.}$$

Hence, below sodium octanoate, for which Q = 8 X 0.065 = 0.52 cal, the sodium salts of fatty acids will have no detergency effect. Long experience confirms this view. It is probable that the same considerations explain the ability of soaps to increase the solubility of hydrocarbons in water [23]. In addition, the removal of solid particles is aided by their peptization by a surface-active substance, i.e. soap [24].

f) The system oil – soap – water is not a simple mechanical mixture, but is bound together by hydrogen bonding and by the energy of the dispersion effect in the given system. In order to establish the energy changes occurring in the formation of these systems, experiments based on the preceding conclusions were carried out.

Soap was wetted with water and then with paraffin oil, and in both cases thermal changes were observed. On the basis of the regularities already observed, we may draw up the following scheme of the formation of the ternary system oil – soap – water:

(oil) ↑ (soap) ↑ (water)

dispersion effect hydrogen bonding

The mechanical properties of these systems, which form the basis of a series of full-bodied lubricants, are associated with the chemistry of their formation. The anhydrous oleogels of oleate and ricinoleate, in combining with two and three molecules of water respectively, lower the limiting shear stress [25]. The further addition of water produces thickening.

g) With respect to heats of wetting, clays [26] vary considerably and give values of Q varying from 0.88 cal (Dubovo kaolin) to 21.0 cal (gumbrin). The heat of wetting is greatly affected by an absorbed cation, and an absorbed cation also greatly affects the amount of bound water (as determined by an independent method).

With respect to their effects on the heats of wetting of clays, absorbed cations can be arranged in the following order:

$$Ca^{++} > H^{+} > Na^{+} > K^{+},$$

whereas the heats of hydration of these cations are in the order:

H —255; Ca —174.5; Na —97; K —77.

The heat of wetting is found to be correlated with the mechanical properties of a clay dough, but since the heat of wetting is determined by the amount of water passing from the free to the bound state, this correlation refers to the amount of bound water A. The limiting shearing stress P_m was determined for different moisture contents of the dough. The measurements were made by means of a conical plastometer. From a series of such experiments Ovcharenko established the following relationship:

$$P_m = A \cdot e^{kc} \text{ or } \log P_m = \log A + kc \cdot \log e,$$

A, of course, can be replaced by Q, the necessary coefficient being introduced (k is an empirical constant).

Absorbed cations greatly affect the mechanical properties of the dough. The cations can be arranged in the same series as that given previously for heats of wetting.

5. In conclusion we will discuss the phenomena observed when water and alcohols penetrate into silica gel.

Many investigators have noted that the heats of wetting of silica gel by lower alcohols are greater than the heat of wetting by water, whereas for higher alcohols the heat of wetting is less than for water. The second statement is readily understandable: the large hydrocarbon radicals cannot penetrate into the narrow pores. The question of why alcohols, such as methanol and ethanol, having small hydrocarbon radicals give heats of wetting higher than that of water remains unresolved [27].

The difficulty with which water penetrates into the pores of silica gel [28] can be explained by the participation of water and silica gel in hydrogen bonding. Water molecules, being capable of two-sided hydrogen bonding:

$$H_2O \ldots\ldots H - O - H \ldots\ldots OH_2$$

may become attached simultaneously to the capillary wall and to other water molecules, and so build a structural formation of molecules within the capillary. Such a formation demands additional mechanical effort for its break-down. Alcohol molecules, which have only one hydrogen bond $CH_3OH \ldots OH_2$ and $C_2H_5OH \ldots OH_2$, can use it either for attaching themselves to the wall of the silica pore or for the formation of a dimer, but they cannot form aggregates attached to the capillary walls. In the wetting of starch, water molecules readily wedge their way into the starch aggregate and can then penetrate still further owing to the mobility (open structure) of the aggregate. Alcohol molecules cannot do this, since they contain hydrophobic hydrocarbon radicals that cannot take part in the "wedging" process. For this reason, the heat of wetting starch with water attains values of greater than 20 cal, whereas the heat of wetting with alcohol scarcely attains 1.6 cal.

We were still further confirmed in this view by the results of Dumansky and Khaflenko [29] on the rheological properties of moist glycerol and sucrose solutions, which were determined by means of a sensitive Shvedov apparatus constructed by these investigators. It was found that neither glycerol nor sucrose solutions are Newtonian liquids. These liquids are made up of hydrogen-bonded molecules, and so have structures that possess shearing moments. A solution of rosin in paraffin oil at the same viscosity is a true Newtonian liquid.

In conclusion we give a quantitative characterization of the concept of hydrophilic character.

The hydrophilic character of the surface or molecule of a high polymer must be determined by the number of active sites (radicals) that become attached to H_2O. We may therefore write:

$$\frac{aM}{18} = n; \; A = 100\,a; \; Q = 80 \cdot a,$$

in which a is the amount (g) of water bound by 1 g of adsorbent, 18 is the molecular weight of water, and n is the number of active centers at which water molecules are attached. In order to determine the value of n, it is essential to know M, the molecular weight of the colloidal substance. When the molecular weight is unknown, one of the following expressions can be considered to characterize the hydrophilic character:

$$M/n = 18/n \text{ or } n/M = n/18$$

The first expression indicates the fraction of the molecular weight corresponding to one active center. The second expression indicates the relative number of active centers in the molecule (micelle) of the colloid. The first quantity diminishes with increase in hydrophilic character, and the second quantity increases.

On the basis of these considerations we may write the following series arranged according to the value of 100 n/M:

Na stearate <	Na palmitate <	Capron <	cellulose <	
0.3	0.4	0.8	0.9-1.3	
silica gel <	starch <	gelatin <	agar	
1.6	1.9	2.3	2.5	

Thus, a detailed study of the wetting of various hydrophilic disperse systems and macromolecular colloids with water has made it possible to calculate that, in the binding of units mass of water by these adsorbents, the amount of heat evolved is always the same, namely 80 cal approximately, i.e. about 1500 cal per mole; this study has enabled us also to obtain a quantitative expression for hydrophilic character. Taking starch and cellulose as examples, we have shown how the rule of "constant heat of formation" can be applied to the solution of various problems relating to the hydrophilic character of systems. It was found to be possible to supplement existing views on the detergency of soap, regarded as the effect of a surface-active substance on the dissolution of hydrocarbons and the peptization of solid particles (soot, dust).

The results of our investigations enable us to regard the phenomenon of wetting as analogous to a chemical process.

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* T. p. = C. B. Translation pagination.

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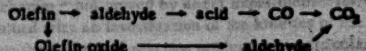
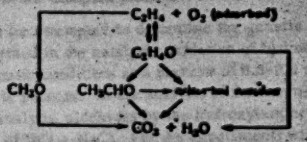
SPECIFICITY OF THE CATALYTIC OXIDATION OF UNSATURATED HYDROCARBONS

L. Ya. Margolis and S. Z. Roginsky

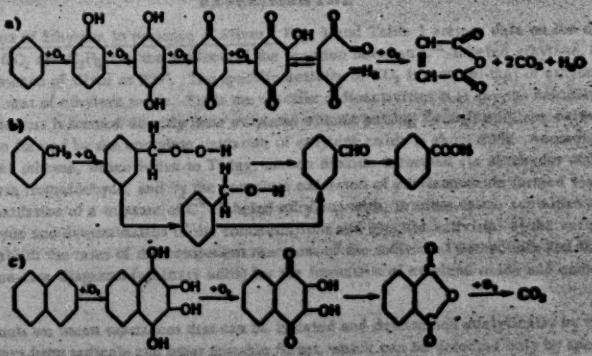
The formation of oxygen-containing products by the direct oxidation of hydrocarbons by molecular oxygen tends to prevent far-reaching oxidation to Co, CO_2, and H_2O with complete breakdown of the carbon skeleton. In the literature [1] the view is firmly held that the main cause of the low specificity of the catalytic oxidation of hydrocarbons is the ready further oxidation and decomposition of the oxygen-containing compounds under the conditions of the synthesis. It is thus usual to represent the oxidation of olefins by the following stepwise scheme:



Twigg [2] proposed a scheme for the oxidation of ethylene in presence of silver in which aldehydes (formaldehyde and acetaldehyde) are intermediate products in the complete oxidation:



Pongratz [3], Sosin [4], and Dolgov [5] consider that the oxidation of aromatic compounds into phthalic anhydride and benzaldehyde proceeds in stages. Naphthalene, for example, is first converted into a naphthol, then into a naphthoquinone, then into phthalic anhydride, and finally into CO_2:



For this reason, in endeavoring to obtain the products of mild oxidation, many investigators have attached great importance to the selection of conditions under which oxygen-containing compounds will be removed rapidly from the reaction zone. There is a considerable basis for ascribing a higher reactivity to organic oxygen compounds than to saturated hydrocarbons, but this is not a general law, and in regard to olefins its applicability is not altogether obvious.

A comparative investigation carried out with two of the principle types of catalysts for mild oxidation — silver and vanadium pentoxide — showed that acetaldehyde and formaldehyde are oxidized considerably more rapidly than propene [6]. It follows that, for olefins also, the low specificity of the processes may be due, in certain cases, to unfavorable relationships between the rates of formation and transformation of intermediate stable oxygen-containing compounds (aldehydes, epoxides, acids), which hinder the accumulation of valuable products. However, this cannot be the only cause, and it cannot be general. Thus, in presence of silver, the oxidation of ethylene oxide — which is practically the only valuable product of the reaction — is slower than the oxidation of ethylene, but the selectivity of the process is nevertheless low owing to considerable formation of CO_2. Over the typical catalyst for the severe oxidation of hydrocarbons (platinum, magnesium and copper chromites, etc.) at 300-400°, aldehydes are oxidized mainly to acids and only partially to CO_2 [7]. Under these conditions both unsaturated and saturated hydrocarbons are oxidized to water and carbon dioxide, and only traces of aldehydes and acids can be detected in the reaction products. These observations give us grounds for a cautious and critical attitude to the accepted stepwise schemes — not proved by direct experiment — for the oxidation of hydrocarbons. The method of labeled atoms combined with an investigation of the kinetics of the process should enable us to establish the genetic relationships between the individual reaction products. In particular, by the introduction of radioactive carbon C^{14} into the reactants — in some cases into the molecule of the original organic compound, and in other cases into the proposed intermediate product of far-reaching oxidation — and by the determination of the distribution of radioactivity among the reaction products, it should be possible to establish the way in which the products arise and the rates of the component reactions of the complex process.

In the present investigation we attempted to determine the genetic relationship between the various stable oxygen-containing compounds formed in the catalytic oxidation of hydrocarbons*. In some of the experiments the oxidation was carried out under static conditions at a pressure of 0.5-0.8 mm, and in others it was carried out under dynamic conditions at atmospheric pressure. In the analysis of the reaction products, CO_2, CO, O_2, and hydrocarbons were determined by volumetric analysis, aldehydes by the hydroxylamine and polarographic methods, and ethylene oxide by absorption in a mixture of HCl + NaCl. For the experiments with labeled molecules, active ethylene [8] and acetaldehyde [9] were prepared by methods developed previously. The radioactivities of the original compounds and isolated reaction products were determined in the form of barium carbonate with end-on counters having mica windows. Typical catalysts for mild oxidation were used: silver and oxides of metals of Groups V and VI of the periodic system.

EXPERIMENTAL

1. Oxidation of Ethylene in presence of Silver. Fig. 1 and Table 1 present data on the distribution of radioactivity between CO_2 and C_2H_4O in the products of the reaction between C^{14}-labeled ethylene, ethylene oxide, and oxygen in presence of silver at 220°. The specific activity of CO_2 is close to that of ethylene and is considerably greater than that of ethylene oxide. From the specific radioactivities it is easy to calculate the proportion of the carbon dioxide that is formed directly from ethylene without passing through ethylene oxide: at 220° it is 80%, and the proportion formed by the complete oxidation of ethylene oxide is about 20%. According to the most generally accepted scheme, which is due to Twigg, carbon dioxide is formed via aldehydes without passing through ethylene oxide, via formaldehyde, and by the complete oxidation of ethylene oxide formed via acetaldehyde (see Scheme 1). By oxidation of a mixture of C^{14}-labeled ethylene with, in some cases, acetaldehyde and, in other cases, formaldehyde and determination of the concentrations and specific activities of the various reaction products, it is possible to establish the rates of the component reactions of the individual compounds and their mixtures. In Fig. 2 we give reaction-rate diagrams (arbitrary units) for the formation of ethylene oxide and carbon dioxide in presence

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* By stable products we mean substances that can be isolated and determined analytically by the usual chemical methods, as distinct from radicals and other unstable forms, which can be detected only by spectrum, magnetic, and other such methods, or by the analysis of indirect kinetic data.

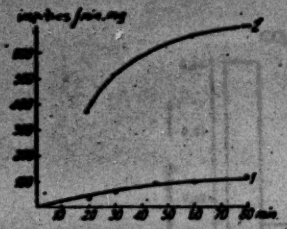


Fig. 1. Variation of the specific radioactivities of ethylene oxide (1) and carbon dioxide (2) during reaction between C^{14}-labeled ethylene, ethylene oxide and oxygen in presence of silver at 220°.

of silver in the oxidation by molecular oxygen of mixtures of ethylene and ethylene oxide, ethylene and acetaldehyde, and ethylene and formaldehyde. In presence of formaldehyde and acetaldehyde the rate of formation of ethylene oxide increases somewhat and the rate of formation of carbon dioxide diminishes. Aldehydes, therefore, do not intensify the formation of carbon dioxide and therefore cannot be the principal intermediaries in the formation of CO_2, either from ethylene without passing through ethylene oxide, or from ethylene oxide itself.

2. Oxidation of Ethylene and Propene in presence of Vanadium Oxides. In the oxidation of ethylene and propene over V_2O_5, the reaction products were shown to contain formaldehyde, acetaldehyde, formic acid, and acetic acid, and also appreciable amounts of carbon monoxide and dioxide. We were

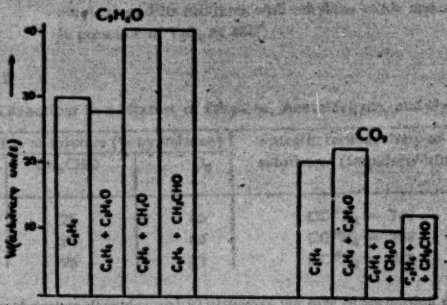


Fig. 2. Reaction-rate diagrams for the formation of ethylene oxide and carbon dioxide in the oxidation of pure ethylene and its mixtures with ethylene oxide and with aldehydes in presence of silver at 220°.

TABLE 1

Temperature (°C)	Time of contact (seconds)	Degree of conversion of ethylene (%)	Specific radioactivity (impulses/min · mg)			Proportion of CO_2 (%) formed from	
			original C_2H_4	C_2H_4O	CO_2	C_2H_4	C_2H_4O
220	3	60	840	120	700	80	20

unable to detect even traces of ethylene oxide and propylene oxide among the reaction products. In order to determine the genetic relationships between the various stable oxygen-containing products, rates of oxidation by molecular oxygen were measured for C^{14}-labeled mixtures of 1) ethylene and ethylene oxide and 2) ethylene and acetaldehyde. The distribution of activity among the various reaction products was determined (see Table 2). It was found (Fig. 3) that the rate of formation of carbon dioxide is not affected by the presence of acetaldehyde in the mixture and is reduced by the presence of ethylene oxide. Consequently: 1) neither acetaldehyde nor ethylene oxide can be a principal intermediate product in the

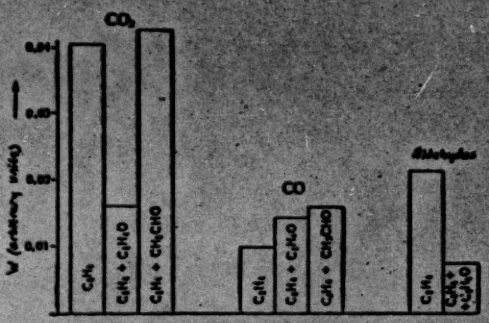


Fig. 3. Reaction-rate diagrams for the formation of aldehydes, carbon monoxide and carbon dioxide in the oxidation of pure ethylene and its mixtures with ethylene oxide and acetaldehyde in presence of V_2O_5 at 400°.

TABLE 2

Oxidation Reactions in a Mixture of Ethylene, Acetaldehyde, and Oxygen over V_2O_5 at 400°

Composition of mixture (% by volume)			Specific radioactivity of original substances (impulses/min · mg)	Specific radioactivity (impulses/min · mg) of	
C_2H_4	CH_3CHO	O_2		CO_2	CO
30	25	45	$CC^{14}H_4 = 740$	556	515
40	20	40	$CC^{14}H_4 = 250$	85	68
28	25	47	$CC^{14}H_4 = 840$	209	208

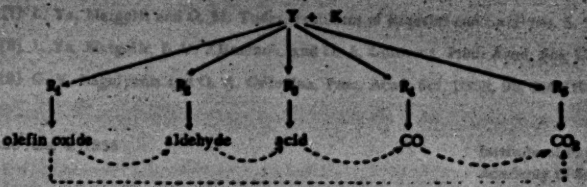
formation of carbon dioxide, and 2) although the rate of formation of carbon monoxide is increased in presence of ethylene oxide and acetaldehyde, radiometry shows that the rate of formation of CO from aldehyde is increased simultaneously, so that there is reason to suppose that both for CO_2 and for CO neither an aldehyde nor ethylene oxide can be the main intermediate product in the reactions.

Under the experimental conditions, there was practically no oxidation of carbon monoxide to carbon dioxide. It was therefore possible to make separate examinations of the origins of these substances. The effect of aldehyde in simultaneously encouraging the formation of CO and discouraging the formation of CO_2 indicates that CO and CO_2 are formed from hydrocarbons by independent parallel routes via unidentified intermediate products.

DISCUSSION OF RESULTS

There is an essential difference between the catalytic actions of silver and vanadium oxides: over silver the addition of oxygen at the double bond with formation of ethylene oxide predominates under certain conditions whereas over vanadium oxides under a wide range of external conditions no olefin oxides can be detected among the reaction products. On the other hand, the formation of aldehydes and acids over V_2O_5 and other oxides (WO_3, MoO_3, etc.) is considerably greater than over silver. In spite of these differences in the composition of the products for oxide catalysts and for silver, the isotope data are very similar in certain respects. For example the further oxidation or decomposition of ethylene oxide over an oxide catalyst or of aldehydes over silver is not the main cause for the absence of these substances among the reaction products. In the oxidation of ethylene over silver and of ethylene and propene over oxides, the successive formation of several stable oxygen compounds either did not occur at all or played a minor part in comparison with their formation in parallel reactions. In the oxidation of hydrocarbons over these catalysts, the formation of carbon dioxide and carbon monoxide also occurs mainly without intermediate formation of

aldehydes and ethylene oxide. Data from the literature and the results of our measurements suggest the following as a likely scheme for the catalytic oxidation of hydrocarbons:



Y being the hydrocarbon, K the catalyst, and R_1 to R_5 labile intermediate products, probably of the peroxide radical type. This conclusion is of great importance for the determination of the direction of further investigations. In order to obtain better results it is first of all necessary to search for catalysts that will direct the reaction into the course desired and to suppress parallel reactions by regulating the chemical composition of the catalyst and varying the conditions of the process. Only then should steps be taken to remove the products of mild oxidation from the reaction zone so that they are isolated without decomposition.

Each of these parallel courses of the oxidation reaction is a complex stepwise process. The kinetic and isotopic data that we have presented lead only to a negative conclusion – that the reactions do not pass through intermediate stable compounds. Positive indications of the nature of the intermediate stages and products are given by the investigation of isotopic exchange, the analysis of the kinetic equations, and some other data. It is likely that the first step is the formation of the singly charged molecular ion O_2^-. The intermediate complex of the determining stage contains O_2^- and, probably, a firmly adsorbed hydrocarbon molecule. Among other intermediate active forms of oxygen are O^- ions and possible also O_3^- ions. Intermediate forms occurring in catalytic oxidation differ substantially from analogous forms occurring in homogeneous oxidation*.

In our investigation we have obtained similar pictures for two hydrocarbons and three oxidizable oxygen compounds. Silver is a typical metal catalyst for mild oxidations, but according to the literature copper and its alloys are in many cases similar to silver. Our results and data in the literature indicate that V_2O_5 is a member of a group of oxide catalysts (WO_3, MoO_3, UO_3, etc.), all of which give similar results. It may be considered, therefore, that the relationships we have found are of fairly wide application, particular to the oxidation processes of aromatic hydrocarbons and alcohols. This view should be verified by the method of radioactive indicators, since all other methods give ambiguous results.

SUMMARY

1. It was shown that, in the oxidation of ethylene over silver, aldehydes cannot be the main intermediate products in the formation of carbon dioxide.

2. It was shown that in presence of V_2O_5 carbon monoxide and dioxide are formed by independent parallel routes, which do not proceed via aldehydes.

3. A probable scheme for the catalytic oxidation of hydrocarbons is given.

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STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 4. DEPENDENCE OF THE STRUCTURE OF SODIUM BOROSILICATE GLASSES ON THE DURATION OF HEATING AT CONSTANT TEMPERATURE

E. A. Porai-Koshits, D. I. Levin, and N. S. Andreev

In previous communications by the first two authors of the present paper and Zhdanov, experimental results were given of a study of the scattering of visible light by sodium borosilicate glasses capable of opalescence and susceptible to leaching [1], the experimental results were presented also on an X-ray and electron-microscope investigation of the structure of the porous products obtained by leaching these glasses [2], and the authors gave their views on the structure of the unleached glasses ("submicroheterogeneous structure") and the causes of their opalescence [3]. According to these views, the increased intensity of light-scattering observed when the temperature of the glasses is raised in the opalescence zone (about 550-700°) is to be explained by the growth of the regions of chemical heterogeneity, which are present even in completely clear glasses, but are then of comparatively small dimensions. The experimental basis for these views was obtained in a comparative study of the structures of porous products obtained by the leaching of opalescent and clear glasses, which were prepared by maintaining samples of glass at temperatures in the opalescence zone and at higher temperatures, respectively.

On the basis of our views it would be expected that the relation between the degree of opalescence of a glass and the structure of the porous product obtained by leaching the glass would be observed also for glasses for which the scattering intensity varies with the duration of heating at constant temperature (in the opalescence zone). The experimental verification of this supposition formed the object of the present investigation.

EXPERIMENTAL

Experimental Procedure

A comparative study was made of the scattering intensities of sodium borosilicate glasses heated at constant temperature (600° or 650°) for various times and of the submicroscopic structures of the porous products obtained from these glasses by leaching; the structures were studied by the method of small-angle scattering of X-rays. The sodium borosilicate glass selected for investigation contained 70 moles % SiO_2, 23 moles % B_2O_3, and 7 moles % Na_2O, this being the most typical of the glasses capable of opalescing and being leached. In order to determine scattering power, samples of glass were prepared in the form of rectangular blocks 9 × 12 × 40 mm, polished on all faces. These samples, and also pieces of glass for X-ray examination, were placed in a muffle furnace and kept there for various times at one of the two fixed temperatures (Table 1).

Constancy of temperature was maintained by means of a thermoregulator. After the period of heating the samples of glass were quenched in the air. The samples obtained at the two different temperatures differed greatly in appearance. The samples quenched from 600° remained clear, only the sample maintained at this temperature for eight hours showing scattering that was scarcely perceptible by the eye. All of the samples quenched from 650° were strongly opalescent, the degree of opalescence increasing considerably with increase in the duration of heating.

This behavior made it necessary to measure the scattering powers of the glasses quenched from the different temperatures by two different methods. The scattering of glasses treated at 600° was measured by a method similar to that described previously [1]*. The scattering coefficients of glasses quenched from 650° could not be measured by the same method because of the occurrence of repeated scattering [1, 4]. Hence, the scattering powers of these glasses were characterized by their transmission coefficients* (i.e. the ratio of the amount of transmitted light to

* The authors thank A. I. Kalyadin for measuring, at their request, the scattering coefficients of glasses quenched from 650°.

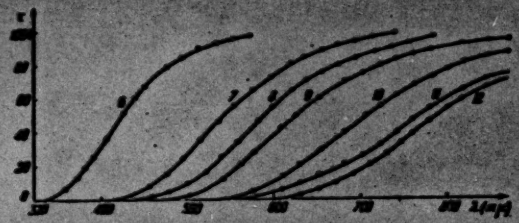

Fig. 1. Transmission coefficient as a function of wavelength for glasses quenched from 650° (Samples 6–12, Table 1).

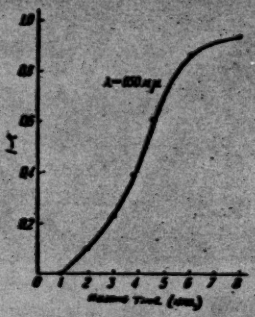

Fig. 2. Scattering power of glass as a function of duration of heating at 650°.

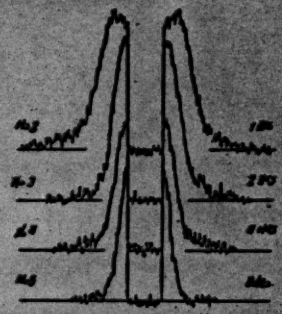

Fig. 3. Microphotometric curves for some samples of porous glasses obtained from glasses quenched from 600° (No. of sample on left; duration of heating (hours) on right).

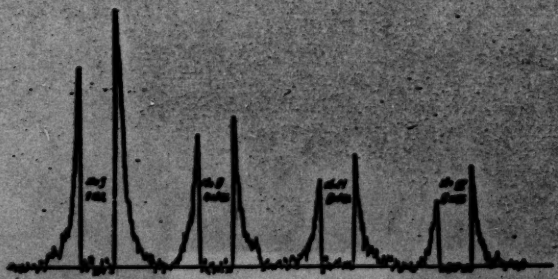

Fig. 4. Microphotometric curves for some samples of porous glasses prepared from glasses quenched from 630°.

TABLE 1

Sample No.	Temperature of heat treatment (°C)	Duration of heating (hours)
1	Unheated glass	
2	600	1
3	600	2
4	600	4
5	600	8
6	650	1
7	650	2
8	650	3
9	650	4
10	650	5
11	650	6
12	650	8

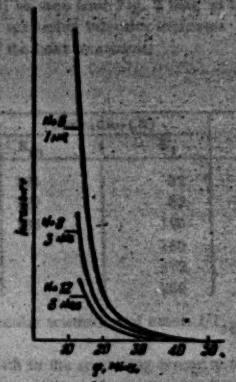

Fig. 5. Intensity of small-angle scattering of X-rays for porous glasses prepared from the original glasses No. 6, 8, and 12.

the amount of incident light). The correctness of this procedure follows from Gurevich's results [5], which show by direct measurement that in sodium borosilicate glasses the absorption of visible light is negligible in comparison with its scattering.

Measurements of transmission coefficients were carried out on an SF-4 photoelectric spectrophotometer. A filament lamp was used as light source. In order to select the most suitable wavelength for comparison of scattering by the glasses (such that the light would be appreciably weakened in all of the samples investigated), transmission-wavelength curves were determined in all of the samples quenched from 650°. These curves are shown in Fig. 1, from which it will be seen that it would be most satisfactory to compare transmission coefficients at a wavelength of 650 mμ.

Glasses for X-ray investigation were ground to a powder of grain size 0.12-0.16 mm and treated with 3 N HCl for 24 hours at a constant temperature of 50°. The leached samples were washed free from residual acid by means of running distilled water, dried, and treated further with 0.5 N KOH for two hours at room temperature. Further rinsing and drying yielded grains of porous glass containing clean channels free from highly dispersed silicic acid. This treatment enabled us to obtain samples of porous glass that gave good small-angle scattering of X-rays. The general features of the structures of the siliceous skeletons of the original glass and the porous product of leaching obtained in this way were determined in previous investigations [2, 3]. The same papers describe the views of the authors concerning the nature of the processes occurring when sodium borosilicate glasses are treated with acids and alkalis.

Small-angle X-ray photographs were obtained in vacuum cameras with CuK_{α} radiation ($\lambda = 1.5418$ Å) rendered monochromatic by reflection from calcite; the distance between sample and plate was 200 mm. Microphotometric measurements were made on the X-ray photographs with the aid of an MF-4 autorecording microphotometer.

Experimental Results

Analysis of our curves for the dependence of the transmission coefficient τ on wavelength (Fig. 1) confirms the result first obtained by Levin and later studied in detail by Gurevich [5]: in sodium borosilicate glasses scattering intensity is proportional to λ^{-n}, n being greater than 4 and, according to Gurevich's results, having a value of about 8. This value is closely in accord with our results, with the exception of results for a narrow spectrum range in the shorter waves, in which n is in the region of 6. This range, however, is narrow, and in the remaining part of the visible spectrum our measurements also give a value of 8 for the index.

In Table 2, Column 6 we give the results of measurements of the intensity of visible scattering by glasses quenched from 600° relative to that of unheated glass No. 1, the scattering intensity of which was 16 times the molecular scattering of ether ($I/I_{ether} = 16$). Fig. 2 shows the dependence of $1-\tau$, which characterizes the

scattering, on the duration of heating at 650°. These results confirm the relation found for the change of scattering in the opalescence zone which we obtained previously [4]. It will be seen from Fig. 2 that, as heating is continued at constant temperature (in the opalescence zone), the scattering intensity increases. The rate of the increase in intensity is the greater, the higher the temperature of the heat treatment.

TABLE 2

Sample No.	Temperature of heat treatment (°C)	Duration of heating (hours)	Pore radius (A)		Relative scattering intensity
			R_m	R_1	
1	Original glass		134	52	1*
2	600	1	129	83	1.4
3	600	2	188	120	3.3
4	660	4		140	3.6
5	600	8		172	9.0
6	650	1		250	

* Scattering intensity of this sample, as compared with the molecular scattering of ether $I/I_{ether} = 16$.

In the preceding communication [3] we explained the growth in the scattering intensity with rise in temperature in the opalescence zone by growth in the regions of heterogeneity — regions of components dispersed through the silica skeleton, which contain boron oxide and sodium silicate. A similar explanation can be given for the growth in the intensity of scattering with increase in the duration of heating. Leaching of the glasses should then give porous glasses of increasing pore size [2, 3], and pore-size measurements should give information concerning the dimensions of the regions of heterogeneity in the original unleached glasses. We carried out such measurements by the method of small angle scattering of X-rays.

Fig. 3 gives microphotometric curves for samples of porous glasses prepared from glasses quenched from 600° (Samples 2-5, Table 1). It will be seen from Fig. 3 that the interference maximum, which can be clearly observed on the curve for Sample 2, moves to smaller scattering angles as heating is prolonged until it disappears behind the trap for the primary beam.

The curves having maxima permitted the determination of the radii of the most frequently occurring pores from the position of the interference maximum ($R = 0.32 \frac{\lambda}{\varphi_m}$) and of the radii of the smallest pores from the slope of the tangent drawn to the curve (log I, φ^2) in the region of the greatest scattering angles; to the remaining curves only the method of tangents was applied [2]. It must be noted that the collimation correction, which is applied to the position of the interference maximum by taking into consideration the final cross-sectional area of the primary beam, was not made, and all pore dimensions determined from the position of the maximum must be considered to be too high by 10-20%. Table 2 gives the results of calculations by both methods: R_m is the radius calculated from the angular position φ_m of the interference maximum, and R_1 is the smallest radius determined from the "tail" of the curve. The results obtained will be discussed below.

The X-rays photographs of porous glasses prepared from glass quenched from 650° were all taken with an exposure of 10 minutes. Both the microphotometric curves (Fig. 4) and the intensity curves (Fig. 5) show that the total intensity of small-angle scattering diminishes with increase in the duration of heating. The duration of heating is indicated by figures on the curves; the other samples gave intermediate curves.

In order to compare the forms of the intensity curves at suitably selected exposures, intensity curves were obtained having identical values for the maximum intensity (i.e. at the least possible scattering angles). Within the limits of error for the determination of very low intensities, the curves for all samples quenched from 650° coincided. The pore radius calculated by the method of tangents is given in the last line of Column 5, Table 2.

Discussion of Experimental Results

The microphotometric curves in Fig. 3 show that with increase in the duration of heating of glass quenched from 600° the interference maximum moves to smaller angles until, finally, the maximum is covered by the trap for the primary beam of X-rays. From this fact we may draw the purely qualitative conclusion that, as heating of the original glass is prolonged, the radius of the most frequently occurring pores of the leached samples increases. The calculated radii of the pores (Table 2) confirm this conclusion. As at the same time there is an increase in

the scattering intensity of the original glasses (Column 6, Table 2), we readily reach the conclusion drawn in previous communications, i.e. that the cause of the increased scattering intensity is the growth, with increased duration of heating at 600°, of the regions of chemical heterogeneity that are present in the glasses.

The rise in the scattering power of the glasses with increase in the duration of heating is still more characteristic of samples quenched from 650°, as will be clear from an examination of Fig. 2. Judging from the preceding results, for these samples also, we should expect a considerable increase in the dimensions of the regions of heterogeneity. However, as indicated above, judging from the X-ray photographs for the corresponding porous glasses, the dimensions of the regions of heterogeneity of all the samples are identical within the experimental error.

This contradiction is only apparent, and it is readily explained when we take into account a feature of behavior that can be derived from Figures 4 and 5: these show that the scattering intensity for X-rays (in the region of scattering angles bounded under the conditions of the experiments by the least possible angle $\varphi_{min} \approx 10'$) falls systematically as the duration of heating of the original glasses is increased. This behavior is quite the reverse of that observed for porous glasses prepared from original glasses quenched from 600°: for these the scattering intensity was the greater, the longer the original glass was maintained at this temperature. The most sensible explanation is therefore that the reduction in intensity observed for Samples 6-12 (Fig. 5) is due to reduction in the number of regions of heterogeneity (in this case pores) having relatively small dimensions (radius less than about 500 A), for the scattering intensity at small angles is proportional to the number of scattering regions of heterogeneity. During the heating there is an increase in the size and number of the larger regions of heterogeneity (radius greater than 500 A) at the expense of the smaller regions, and after the leaching the sample contains mainly large pores, the scattering by which — owing to the inadequate resolving power of the apparatus at our disposal — falls in the region covered by the trap for the primary beam.

Hence, the observed reduction in the intensity of X-ray scattering (Fig. 4) does not contradict the views previously advanced by the authors [2, 3], according to which increase in the intensity of light scattering is to be explained by the growth of the regions of heterogeneity, which, in their turn, determine the formation of more coarsely porous glasses. The immediate problem in the investigation of sodium borosilicate glasses capable of showing opalescence is the improvement of the procedure for measuring X-ray scattering at small angles so that the upper limit of the size of regions of heterogeneity — which apparently lies close to the wavelength of visible light — may be found. The solution of this problem is of fundamental interest not only for a more accurate determination of the structure of sodium borosilicate glasses, but also for the theory of scattering by turbid media.

SUMMARY

1. The intensity of the scattering of light by sodium borosilicate glasses increases with increase in the duration of heating at constant temperature in the opalescence zone.

2. When the glasses are heated at constant temperature in the opalescence zone, the pore size of the porous glasses obtained by the leaching of the heated glasses increases.

3. The increase in the intensity of light scattering with increase in duration of heating at constant temperature in the opalescence zone is to be explained by growth of the regions of chemical heterogeneity present in sodium borosilicate glasses, a view that is confirmed by an examination of the submicroscopic structure.

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SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 11. CHARACTERIZATION OF THE SOLID PHASES OF THE SYSTEM LiOH – H_2O_2–H_2O BY THERMAL ANALYSIS

S. Z. Makarov and T. A. Dobrynina

Compounds of lithium peroxide with hydrogen peroxide and water have received little study. The first compound of this type $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ was prepared by de Forcrand [1] by the action of hydrogen peroxide on aqueous-alcoholic solutions of lithium hydroxide. According to de Forcrand's results, the decomposition of $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ in the cold in a vacuum over phosphoric oxide for 36 days occurs with simultaneous loss of water and hydrogen peroxide and formation of anhydrous lithium peroxide. Pierron [2] was unable to confirm de Forcrand's results. In the dehydration of the compound $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ in a vacuum over phosphoric oxide, Pierron obtained a preparation of composition $Li_2O_2 \cdot 0.18H_2O_2 \cdot 3.09H_2O$.

Agunzi [3] showed that, when $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ is heated for six hours in a vacuum over phosphoric oxide at the temperature of boiling ether, it loses its water completely and also 0.4 of a molecular proportion of hydrogen peroxide; he concluded that in hydrates of perhydrates water is bound less firmly than hydrogen peroxide. Agunzi explained the results obtained by de Forcrand [1] by the prolonged drying of the $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$. Cohen [4] treated a suspension of lithium ethoxide in absolute ethanol with 30% hydrogen peroxide and obtained a compound which he characterized as the monohydrate of lithium hydroperoxide $LiOOH \cdot H_2O$. An X-ray structure analysis carried out by Cohen on his preparation of $LiOOH \cdot H_2O$ and on preparations obtained by de Forcrand's [1] and Pierron's [2] methods showed that they were all the same substance. Cohen, therefore, denied the existence not only of $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, but also of lithium peroxide compounds of the perhydrate type in general. According to Cohen, lithium hydroperoxide is stable only when in equilibrium with the mother solution, but is unstable after being dried; it can be preserved for a short time in an open vessel if cooling is applied. By the vacuum drying of lithium hydroperoxide monohydrate over phosphoric oxide at 20 mmfor 18 days, Cohen obtained a preparation containing 99% of Li_2O_2.

In spite of Cohen's observations, Feher [5] noted that the phase $Li_2O_2 \cdot H_2O_2$ or LiOOH, i.e. anhydrous lithium hydroperoxide, gives a clearly defined Debye diagram. Cohen [4] assigns the compound $LiOOH \cdot H_2O$ to the rhombic syngony and gives the following values for the parameters of its crystal lattice: a = 7.92 A; b = 9.52 A; c = 3.20 A. According to Cohen the density of $LiOOH \cdot H_2O$ is $d_{calc} = 1.60$, $d^{25}_{expt} = 1.69$. The refractive indices for the $LiOOH \cdot H_2O$ crystal, determined by the immersion method, are $\alpha = 1.458$ and $\gamma = 1.526$.

A study that we made [6] of the solubility isotherms of the system $LiOH–H_2O_2–H_2O$ showed the existence of lithium peroxide perhydrates of composition: $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ ($LiOOH \cdot H_2O$ according to Cohen), and $Li_2O_2 \cdot 2H_2O_2$. The compounds $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$, $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, and $Li_2O_2 \cdot 2H_2O_2$ have been isolated and studied by the method of thermal analysis.

The heating curves for the preparations of $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ coincided, although solubility isotherms in the system $LiOH–H_2O_2–H_2O$ clearly indicate the existence of two individual hydrates of lithium peroxide monoperhydrate $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ [6]. It may be supposed that the phase $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ has a high vapor pressure and exists only in equilibrium with the mother solution. The individuality of the compounds $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and $Li_2O_2 \cdot 2H_2O_2$ was confirmed by X-ray qualitative phase analysis, which was carried out by G. A. Goldee.

EXPERIMENTAL

The thermal decomposition of lithium peroxide perhydrates was investigated by the method of differential heating curves with a photorecording Kurnakov pyrometer. The samples under investigation were placed in pyrix test tubes or Stepanov vessels. The exit tube of the Stepanov vessel was connected through an absorption vessel

containing sulfuric acid to a measuring buret, which permitted the volume of gas evolved in the thermal decomposition of lithium peroxide perhydrates to be measured quantitatively. The samples were heated at a rate of 4-6° per minute. In the determination of the heating curves with the pyrometer, samples weighing 0.2-0.5 g were taken of the limiting peroxide perhydrates.

In the study of the thermal decomposition of lithium peroxide perhydrates in Stepanov vessels, the curves obtained for gas evolution as a function of time were superimposed on the corresponding heating curves, so that it was possible to determine which thermal effect corresponded to the evolution of oxygen.

Thermal Analysis of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$. Fig. 1 shows the heating curve for $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ determined in an open Pyrex test tube. Under these conditions the thermal decomposition of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ is characterized by two well defined endothermic effects, which begin at 85° and 310°, and by a small one at 65°. On the differential heating curve there is a small inflection at 95°. In order to interpret the thermal effects obtained, samples of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ were heated in a furnace to the required temperature and then analyzed for content of lithium and active oxygen. The lithium content was determined from the alkalinity (titration with 0.1 N H_2SO_4), and active oxygen by titration with 0.1 N $KMnO_4$ in acid solution. The results for the thermal decomposition of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ in an open vessel are given in Table 1.

TABLE 1

Change in Composition in the Heating of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ in an Open Vessel

Temperature (°C)	Composition of preparation obtained (%)						
	$\frac{1}{2}O_2$	Li	Li_2O_2	H_2O_2	H_2O	LiOH	$Li_2O_2 : H_2O_2 : H_2O$
—	26.08	11.68	38.60	26.83	34.57	—	1 : 0.94 : 2.29
100	26.06	11.39	37.63	27.55	34.82	—	1 : 0.99 : 2.36
170	29.59	26.58	84.83	—	11.96	3.21	1 : 0 : 0.36
310	29.69	27.72	85.12	—	8.05	6.83	1 : 0 : 0.24
320	28.38	28.07	81.37	—	6.69	11.94	1 : 0 : 0.21

TABLE 2

Data on the Evolution of Oxygen in the Thermal Decomposition of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$

Duration of experiment (minutes)	Amount of oxygen (cc)	Duration of experiment (minutes)	Amount of oxygen (cc)	Duration of experiment (minutes)	Amount of oxygen (cc)	Duration of experiment (minutes)	Amount of oxygen (cc)
26	0.17	45	27.46	66	30.74	87	46.97
27	0.51	48	28.32	69	33.50	90	49.56
30	3.45	51	28.32	72	36.26	93	51.11
33	8.81	54	28.32	75	39.72	96	52.84
36	15.37	57	28.32	78	41.79	99	55.08
39	22.45	60	29.18	81	42.48	102	55.43
42	26.47	63	29.36	84	44.21	103	55.43

TABLE 3

Data for the Interpretation of the Heating Curve of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, determined in a Stepanov Vessel

Temperature (°C)	Composition of the resulting preparation (%)						
	$\frac{1}{2}O_2$	Li	Li_2O_2	H_2O_2	H_2O	LiOH	$Li_2O_2 : H_2O_2 : H_2O$
—	28.73	12.10	39.98	31.44	28.58	—	1 : 1.06 : 1.92
110	22.69	13.52	44.66	15.14	40.20	—	1 : 0.48 : 2.99
150	18.79	20.60	53.37	—	31.25	14.87	1 : 0 : 1.37
175	21.09	21.31	0.46	—	29.60	10.45	1 : 0 : 1.23
220	8.80	29.02	34.37	—	0.94	74.89	1 : 0 : 0.09

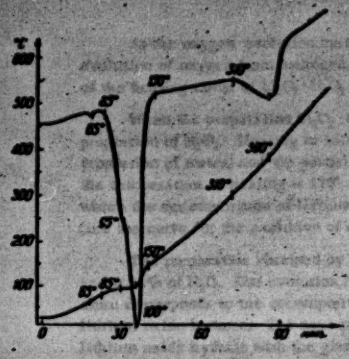

Fig. 1.

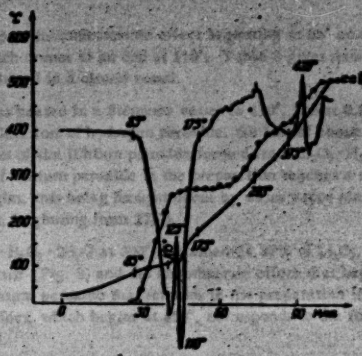

Fig. 2.

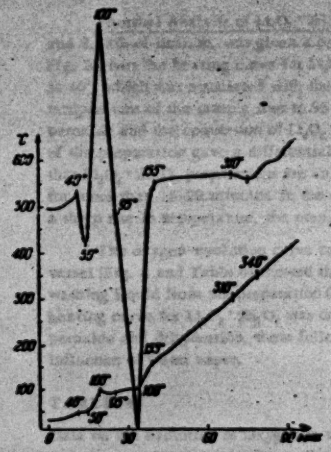

Fig. 3.

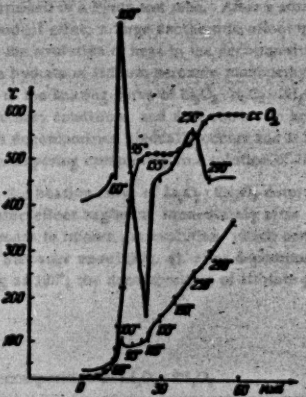

Fig. 4.

As will be seen from Table 1, in the temperature range 100–170° the preparation $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ loses all of its hydrogen peroxide and almost all of its water, and is converted into 85% lithium peroxide. Up to 310° lithium peroxide is stable. Heating to 320° results in the partial loss of its active oxygen. Thus, the endothermic effect on the heating curve of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ in the range 85–100° corresponds to the separation of hydrogen peroxide and water. The inflection on the differential curve at 95° corresponds to the superposition of the exothermic effect of the decomposition of hydrogen peroxide on the endothermic effect of dehydration. The endothermic effect at 65° corresponds to the removal of mother liquor from the $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ preparation. It was shown previously that Li_2O_2 decomposes at 318–320° [7] and the second endothermic effect on the heating curve (310°) corresponds to the decomposition of lithium peroxide formed from $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$.

In order to characterize the process of oxygen evolution from $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, a heating curve was determined in a hermetically sealed Stepanov vessel. The resulting heating curves and the curve for oxygen evolution are shown in Fig. 2. Table 2 gives the data from which the gas-evolution curve was constructed.

As the oxygen-evolution curve in Fig. 2 shows, the endothermic effect beginning at 85° corresponds to intense evolution of oxygen from hydrogen peroxide, which comes to an end at 110°. Table 3 gives data for the interpretation of the heating curve of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, determined in a closed vessel.

When the preparation $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ was heated in a Stepanov vessel to 110°, it lost 0.60 of a molecular proportion of H_2O_2. Heating to 150° led to complete loss of hydrogen peroxide, the loss of about one molecular proportion of water, and the partial decomposition of the lithium peroxide formed from $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$. When the temperature of heating is 175°, the content of lithium peroxide in the preparation reaches a maximum, after which the decomposition of lithium peroxide begins, this being brought about by water vapor present in the vessel (see the curve for the evolution of oxygen, Fig. 2, beginning from 175°).

The preparation obtained by heating $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ at 320° contained 24.37% of Li_2O_2, 74.69% of LiOH, and 0.94% of H_2O. Gas evolution from 318° onward (Fig. 2) and the endothermic effect that begins at this temperature corresponds to the decomposition of the lithium peroxide that remains in the preparation in admixture with lithium oxide hydrate. The next endothermic effect, which begins at 420°, corresponds to the fusion of the lithium oxide hydrate with the glass of the vessel.

The heating curve determined for $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ in a closed Stepanov vessel differs somewhat from the heating curve determined in an open Pyrex test tube. This is to be explained by the decomposition of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ when heated in a closed vessel and the action of water vapor on the lithium peroxide formed.

Thermal Analysis of $Li_2O_2 \cdot 2H_2O_2$. The $Li_2O_2 \cdot 2H_2O_2$ preparation, which contained 35.04% of active oxygen and 6.78% of lithium, was given a preliminary wash with ether to remove the mother liquor that it contained. Fig. 3 gives the heating curve for $Li_2O_2 \cdot 2H_2O$, determined in a Pyrex test tube. After a small endothermic effect at 40°, which was associated with the removal of residual ether, a large exothermic effect quickly followed. The temperature of the sample rose to 95-100° owing to the evolution of heat in the decomposition of hydrogen peroxide and the conversion of $Li_2O_2 \cdot 2H_2O_2$ into the hydrate of lithium peroxide monoperhydrate. Further heating of the preparation gave a differential curve similar to the heating curve of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$. It must be mentioned that $Li_2O_2 \cdot 2H_2O_2$ preparations are unstable under ordinary conditions, and they cannot be kept at room temperature for more than 15-20 minutes, in the course of which decomposition gradually occurs and is finally accompanied by a sharp rise in temperature, the preparation then decomposing completely to a solution of lithium hydroxide.

The oxygen-evolution curve corresponding to the heating curve of $Li_2O_2 \cdot 2H_2O_2$ determined in a Stepanov vessel (Fig. 4 and Table 4) showed that the exothermic effect beginning immediately after the removal of the washing liquid from the preparation (50-60°) corresponds to intense gas evolution, which continues to 110°. When the heating curve for $Li_2O_2 \cdot 2H_2O_2$ was determined in a Stepanov vessel (Fig. 4), after decomposition of hydrogen peroxide and dehydration, these followed, beginning at 190°, the decomposition of lithium peroxide under the influence of water vapor.

TABLE 4

Data on the Evolution of Oxygen in the Thermal Decomposition of $Li_2O_2 \cdot 2H_2O_2$

Duration of experiment (minutes)	Amount of oxygen (cc)	Duration of experiment (minutes)	Amount of oxygen (cc)	Duration of experiment (minutes)	Amount of oxygen (cc)	Duration of experiment (minutes)	Amount of oxygen (cc)
1	0.17	14	13.05	30	55.16	48	64.38
3	0.35	15	28.97	33	55.16	51	65.07
6	0.87	18	43.50	36	56.38	54	65.07
9	1.91	21	53.42	39	57.59	57	65.07
12	4.52	24	55.16	42	60.03	60	65.07
13	7.31	27	55.16	45	62.71		

SUMMARY

1. Study of the thermal decomposition of $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and $LiO_2 \cdot 2H_2O_2$ showed that, when these compounds are heated to 150-170°, they are converted into Li_2O_2 with simultaneous loss of H_2O_2 and H_2O.

2. The simultaneous loss of H_2O_2 and H_2O by the preparation $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$ and its conversion by heat into Li_2O_2 give grounds for assigning a perhydrate structure to this compound, i.e. $Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$, and not the hydroperoxide $LiOOH \cdot H_2O$.

3. The compound $Li_2O_2 \cdot 2H_2O_2$ was isolated for the first time, and its individuality was confirmed by the thermal method.

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PHYSICOCHEMICAL STUDY OF THE SYSTEM SODIUM SUPEROXIDE – SODIUM OXIDE

T. V. Rode and G. A. Golder

Sodium Peroxide (Na_2O_2) was first prepared in 1810 [1, 2] by heating sodium in an atmosphere of oxygen; its composition was determined in 1839 [3], and later confirmed in 1862 [4]. According to some data [5-7] sodium peroxide melts at about 460° without decomposition, which sets in only in the liquid state when heating is continued further; but according to other data [8, 9] it decomposes in the solid state. Sodium peroxide greedily absorbs moisture and carbon dioxide from the air, and at high temperatures it reacts with most metals [5, 6] and with various oxides [10-12] and silicates [13].

Sodium Superoxide (NaO_2) was first synthesized in 1936 by Kazarnovsky [14]. From 1948 onward Kleinberg and coworkers published a series of papers on the synthesis, analysis, and magnetic behavior of NaO_2 [15-17], and then on the reactions of NaO_2 and KO_2 with the nitrates of various metals in liquid ammonia [18, 19].

Kazarnovsky [14], Templeton and Bauben [20], and Zhdanov and Zvonkova [21] ascribe a cubic structure of the NaCl type of sodium superoxide.

Later, Carter and Templeton [22] found, by X-ray analysis of a monocrystal, that at room temperature NaO_2 has a disordered structure of the pyrite type, the parameter of which was found by Zhdanov and Zvonkova [21] to be 5.44 A.

In 1953 one of us [23] showed by the method of differential thermal analysis that sodium superperoxide has two low-temperature polymorphous modifications with transitions at −80° and −43°. At these temperatures the differential cooling curves showed two reversible exothermic effects that could be explained by these transitions. We detected similar effects for KO_2. In the same year three papers [22, 24, 25] appeared which confirmed our results on the existence of two low-temperature modifications of NaO_2 by other methods. Thus, in the article by Zhdanov [24], which reviews X-ray investigations carried out in his laboratory, it is stated that two phase transitions of NaO_2 at about − 70° and −40° were established by the method of low-temperature X-ray analysis described by Golder [26], and X-ray powder photographs are given for these temperature ranges. Todd [25] found two maxima at −77° and −50° on the curve for heat capacity plotted against temperature which can be explained by these transitions, and Carter and Templeton [22] determined the structures of these low-temperature modifications: NaO_2 in the form that exists below −80° has the structure of marcasite with the parameters a= 4.26 A, b= 5.54 A, and c= 3.44 A; NaO_2 in the form existing between −80° and −43° has a pyrite structure with the parameter a= 5.46 A; and, as stated above, at above −43° NaO_2 has a disordered pyrite structure. At −80°, i.e., at the transition temperature, Neiding and Kazarnovsky [27] found a maximum on the curve for the dependence of magnetic susceptibility on temperature.

The transition temperatures given by various authors vary from −70° [24] to −80° [23] and from −40° [24] to −50° [22, 25]. The entropy of Na_2O is 27.9 cal/ mole· degree at 298.16°K [25]. The specific heat of NaO_2 has been measured at various temperatures by Vedenеev and Skuratov [28] and by Todd [25].

The question of the existence of the compound Na_2O_3 still remains open. Joannis [29] states that he obtained Na_2O_3 in admixture with sodium peroxide by oxidizing a solution of sodium in liquid ammonia, but de Forcrand [30] and Kraus and Whyte [31] have thrown some doubt on Joannis' results.

By tensimetric analysis, Raikhshtein and Kazarnovsky [31, 33] have shown that no intermediate potassium trioxide (K_2O_3) is formed in the thermal decomposition of potassium superoxide. In the present investigation it is shown that no compound of composition Na_2O_3 is formed in the thermal decomposition of NaO_2, but this does not enable us to deny altogether the possibility of its existence under other conditions. By way of example we may cite chromium dioxide [34], which is not formed in the thermal decomposition of chromic anhydride under the usual conditions, but can be obtained at high pressures.

EXPERIMENTAL

We have carried out a physicochemical investigation (chemical, thermal, and X-ray analyses, determination of composition-temperature curves and decomposition polytherms) on sodium peroxide and superoxide, and we have obtained the composition-temperature diagram for the system $NaO_2 - Na_2O$. The decomposition polytherms were determined both by continuous measurements of loss in weight on a thermobalance and also by volumetric measurement of the oxygen evolved during the recording of the thermograms.

A detailed description of the prodcedure is given in previous papers [35, 36]. All the weighed samples for investigation were taken in a chamber in which the air was purified from moisture and carbon dioxide by means of suitable absorbents (P_2O_5, Na_2O_2, and KO_2). In the course of work with these samples, they were again isolated from the action of moisture and atmospheric carbon dioxide.

Investigation of Sodium Peroxide

The sodium peroxide preparation taken for investigation had the composition Na_2O_2 97.52%, NaOH 1.49%, and Na_2CO_3 0.99%. As this preparation contained 1.49% of hydroxide impurity, which could itself give thermal effects, we determined the differential thermogram of NaOH, which is shown in Fig. 1. The following heat effects a are to be observed on the thermogram. There is an effect at 60-65°, due to the fusion of sodium hydroxide monohydrate, observed visually. This effect is not accompanied by change of composition, this fact being shown by the curve for weight loss against temperature, which we determined by continuous weighing of the sample on a thermobalance during heating. Beginning from 123° the thermogram shows a drawn-out endothermic effect having a gentle maximum; this effect corresponds to the continuous removal of water from the melt. On the curve for weight loss against temperature, beginning from 124°, i.e. in the region of this effect, a loss in weight is observed, which confirms that the effect corresponds to removal of water from the substance. There are then two large superimposed effects on the thermogram at 280-295° and 305-314°. The first of these corresponds to the transition of the α-modification of NaOH into the β-modification, and the second corresponds to the melting of the β-modification [37]. The results of Smothers and coworkers [38] on the thermal analysis of sodium hydroxide are close to those obtained by us.

Fig. 2 shows the differential thermogram for sodium peroxide (Curve 1) and the simultaneously determined (from the volume of evolved oxygen) decomposition polytherm (Curve 2). The abscissas on both curves represent time (minutes), and the ordinates are: Curve 1, temperature difference between sample and standard (magnesium oxide) and Curve 2, milliliters of oxygen evolved in the given interval of time, reduced to standard conditions (STP).

On the thermogram for sodium peroxide (Fig. 2, Curve 1) there are at first two small endothermic effects, beginning at 275° and 287°. These effects are analogous to those on the NaOH thermogram (Fig. 1) and correspond to a polymorphous change followed by melting of the impurity. The lowering of the melting point of the hydroxide is probably due to the fact that it is not now present in the pure state, but only as an impurity in Na_2O_2. Further along the thermogram (Fig. 2) there is an endothermic effect at 510° corresponding to the melting of the peroxide. In the literature either a lower melting point of 460° is reported [5, 6], or it is stated that the peroxide does not melt, but decomposes [8, 9]. The decomposition polytherms (Fig. 2, Curve 2) show that at first, approximately from 380° to 510° (section a-b), there is only slight decomposition of solid peroxide with evolution of oxygen (about 0.02 atom per molecule). At 510° Na_2O_2 melts, as indicated by the endothermic effect on the thermogram. The slow decomposition of the peroxide continues also in the liquid state up to about 535° (Curve 2, section b-c), after which the rate of decomposition increases (section c-d) until at 545° vigorous evolution of the remaining active oxygen occurs with formation of solid sodium oxide (section d-e). Corresponding to this last process there is an endothermic effect beginning at 545° on the thermogram (Fig. 2, Curve 1). This effect passes over into an exothermic effect, and we have shown that this arises from interaction between the oxide formed and the Pyrex glass of the vessel. We have observed a similar process in an investigation of Li_2O_2 [35, 36]. The occurrence of an analogous effect when the thermogram is determined in a stainless steel beaker showed that Na_2O, unlike Li_2O [35, 36], reacts not only with glass, but also with stainless steel, and only by the use of nickel beakers was it found possible to avoid any interaction, as indicated by the associated exothermic effect on the thermograms.

Investigation of Sodium Superoxide

The compositions of the sodium superoxide preparations studied were:

No.	NaO_2 (%)	Na_2O_2 (%)	NaOH + Na_2CO_3 (%)
1	76.60	21.95	1.55
2	86.63	12.88	1.89

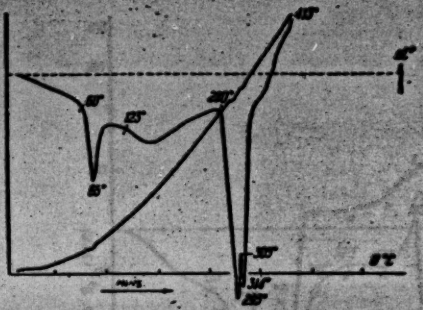

Fig. 1. Thermogram of sodium hydroxide.

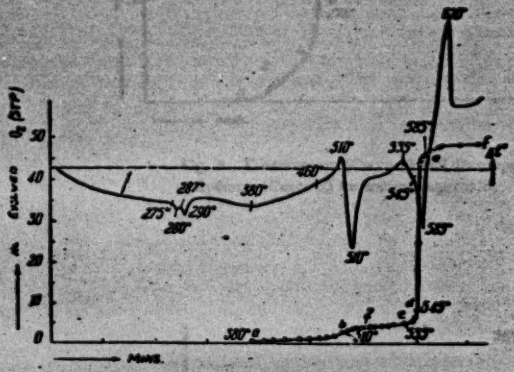

Fig. 2. Thermogram (Curve 1) and decomposition polytherm (Curve 2) for sodium peroxide.

Since sodium peroxide is a decomposition product of the superoxide, its presence does not affect the form of the thermograms obtained. In the X-ray photographs obtained from both of the original preparations both NaO_2 lines and Na_2O_2 lines were observed. The compositions given later for intermediate decomposition products (ranging down to Na_2O_2) are referred by calculation to pure sodium superoxide.

Fig. 3 gives the thermogram and decomposition polytherm for Preparation No. 1, and Fig. 4 gives these curves for Preparation No. 2. On the thermogram for Preparation No. 1 (Fig. 3, Curve 1), the following effects are observed. At about 120° a fairly large endothermic effect begins; it corresponds to the decomposition of NaO_2 with formation of a continuous series of solid solutions up to a limiting composition corresponding to $Na_2O_{2.05}$; this follows from the continuous course of the decomposition polytherm for sodium superoxide as far as the composition indicated in the section a-b (Curve 2). X-ray investigations on Preparation No. 2 before and after being heated in a Stepanov vessel for 26 hours in the vapor of boiling xylene (138°), i.e., at a temperature corresponding to the field of existence of these solid solutions, showed a small shift in the interference lines (see Table 1), which confirmed the results of polythermal analysis.

Table 1 shows that there is a reduction in the parameters of the elementary cell, which corresponds to the formation of "deficiency" solid solutions, which is exactly what occurs in the present case.

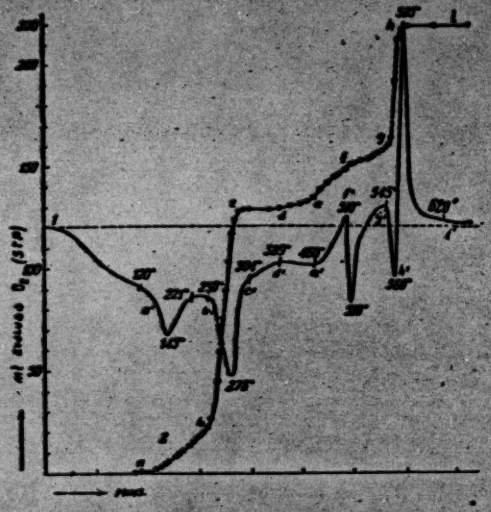

Fig. 3. Thermogram (Curve 1) and decomposition polytherm (Curve 2) for sodium superoxide.

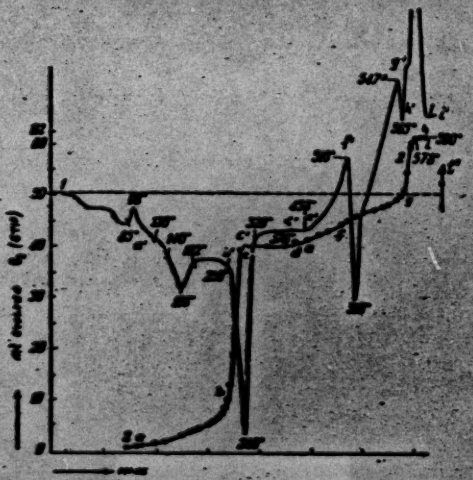

Fig. 4. Thermogram (Curve 1) and decomposition polytherm (Curve 2) for sodium superoxide.

TABLE 1

Interplanar Distances of Preparation No. 2 Before and After Being Heated at 138°

Interplanar Distances d		Difference	
Original superoxide	After being heated at 138°	Absolute	Relative (%)
3.0739	3.0636	0.0103	3.3
2.7670	2.7559	0.0111	4.0
2.5689	2.5571	0.0118	4.6
1.9584	1.9406	0.0158	8.1
1.8211	1.8054	0.0157	8.6
1.6698	1.6475	0.0138	8.3
1.5976	1.5834	0.0142	9.1
1.2701	1.2586	0.0115	9.6
1.0607	1.0470	0.0137	12.9

The thermogram (Fig. 3, Curve 1) shows that, beginning at 250°, there is a second large endothermic effect, which is accompanied by vigorous evolution of oxygen. The almost vertical section b-c on the decomposition polytherm (Curve 2), which is found in the region of this effect, indicates that the effect corresponds to the decomposition of the solid solution of limiting composition to Na_2O_2. Chemical analyses on the products formed by heating sodium superoxide above 320°, i.e. above the temperature of the effect under consideration, confirm that the decomposition product is sodium peroxide. Moreover, on X-ray powder photographs the superoxide lines disappear and only lines due to sodium peroxide remain. We observed no effects on the thermograms and no retardation on the decomposition polytherms in the region of the composition Na_2O_3. This indicates that, in the thermal decomposition of NaO_2, no compound of composition Na_2O_3 is formed, the limiting solid solution $Na_2O_{2.60}$ being decomposed directly to Na_2O_2.

Above 380° slow evolution of oxygen from sodium peroxide begins (section d-e, Curve 2). This evolution is not accompanied by any appreciable thermal effect. At about 460° (point e, Curve 2) there is an increase in the rate of oxygen evolution, and from this temperature onward sodium oxide, formed by decomposition of the peroxide, reacts, as we have shown, with the Pyrex glass of the vessel. On the thermogram this process corresponds to a small exothermic effect at 460-510°. At 510° the thermogram shows a large endothermic effect due to the fusion of undecomposed Na_2O_2. Between 510° and 545° the decomposition of the peroxide continues in the fused state (section f-g, Curve 2). At 545° the thermogram shows an endothermic effect and the decomposition polytherm indicates a second vigorous evolution of gas (section g-h); this effect conesponds to the decomposition of the remaining melt with evolution of the whole of the active oxygen and formation of solid Na_2O.

This effect passes over immediately into a large exothermic effect at 560-585°, which corresponds to interaction between the sodium oxide formed and the Pyrex glass of the vessel, as we have established previously in the investigation of Na_2O_2.

Fig. 4 shows the thermogram (Curve 1) and decomposition polytherm (Curve 2) for sodium superoxide preparation No. 2. Comparison of the thermograms for the two preparations (Curve 1, Fig. 3 and Curve 1, Fig. 4) shows that there is an additional small exothermic effect at 85-95° on the thermogram of the second preparation (Fig. 4).

The X-ray diagram of a preparation maintained at 100° for two hours showed that it was still the same sodium superoxide but in the form of considerably larger crystals, this fact being indicated by breaks in the continuity of the interference lines of the X-ray powder photograph. This implies that the exothermic effect found at 85-95° (Fig. 4) corresponds to the coarsening of the crystals of NaO_2. In the remaining sections of the thermograms and decomposition polytherms Preparations No. 1 and 2 behave almost identically. A certain difference is observed in that the large exothermic effect due to the interaction between the sodium oxide formed and the Pyrex glass of the vessel begins in preparation No. 2 immediately after the fusion effect, and the endothermic effect corresponding to the vigorous decomposition of the residual peroxide melt (occurring here at 547°) is, as it were, wedged into the large exothermic effect.

The overall composition of preparations at the point of fusion (516°) was found to vary fairly considerably, namely from $Na_2O_{1.88}$ (for the original Na_2O_2) to $Na_2O_{1.72}$ (for the peroxide preparation obtained by heating superoxide No. 2), but the melting point remained almost constant. This indicates constancy in the composition of the liquid phase, corresponding to the composition Na_2O_2.

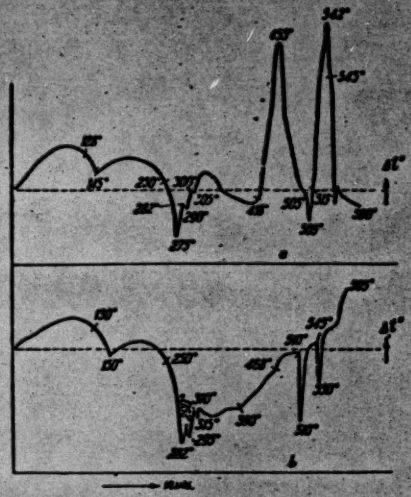

Fig. 5. Thermograms for sodium superoxide recorded without protection from atmospheric moisture: a) in a quartz beaker: b) in a nickel beaker.

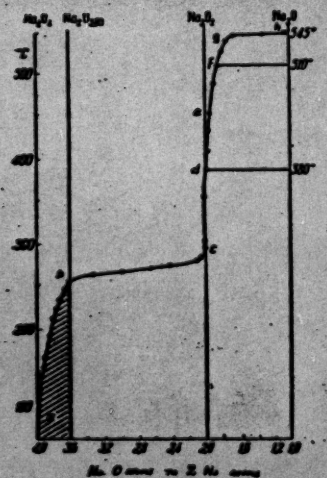

Fig. 6. Composition-temperature diagram for the system NaO_2—Na_2O obtained at a rate of heating of 5.5–6° per minute.

Fig. 5 gives two thermograms recorded in open beakers without protection from atmospheric moisture and carbon dioxide. The first (Fig. 5 a) was obtained in a quartz beaker, and the second (Fig. 5 b) in a nickel beaker. In both thermograms, in addition to the usual effects for NaO_2 at about 130° and at 250°, there were two small endothermic effects at 282° and 300° and at 290° and 310°, respectively. These effects correspond to the polymorphous change and subsequent fusion of NaOH impurity formed by reaction of the preparation with atmospheric moisture, as we have shown previously in the investigation of Na_2O_2. These effects were not observed on thermograms recorded in Stepanov vessels (Fig. 3 and 4, since the samples were then isolated from the effect of atmospheric moisture.

In Fig. 5 a there are two large exothermic effects beginning at 418° and 513° which are absent in Fig. 5b. The first of these effects corresponds to interaction between the glass of the vessel and NaOH impurity formed by heating NaO_2 in presence of atmospheric moisture, and the second corresponds to interaction between the glass and sodium oxide formed by the decomposition of residual peroxide. These effects are not observed on the thermogram recorded in open nickel beakers (Fig. 5 b), since neither NaOH [37] nor Na_2O reacts with nickel. This thermogram shows that they do not react even at high temperatures.

The Na_2O_2 fusion effect occurs at 510° in Fig. 5 b and at 505° in Fig. 5 a. The lowering of melting point when the thermogram was recorded in an open quartz beaker is probably due to the admixture of the sodium silicate formed.

A comparison of curves for weight loss as a function of temperature determined continuously with the aid of a thermobalance for the superoxide heated 1) in a current of dry oxygen and 2) in an atmosphere of dry CO_2-free air showed that air lowers the decomposition temperature both of NaO_2 itself and of the intermediate products.

On thermograms recorded in Stepanov vessels the decomposition temperatures are close to those obtained in a stream of oxygen. The explanation is that, during the determination, the samples are in an atmosphere of the oxygen evolved in the decomposition of the preparations, which displaces the air initially present in the vessels.

Composition-Temperature Diagram for the System Sodium Superoxide – Sodium Oxide

Apart from the above-described investigations, we have determined the composition-temperature diagram for the system NaO_2–Na_2O. Weighed samples of NaO_2 preparations were heated in Stepanov vessels to temperatures ranging from 150° to 565°, thermograms and oxygen evolution being simultaneously recorded. When the thermograms had been recorded, the products were analyzed for active oxygen. X-ray diffraction photographs were taken of some of the samples.

TABLE 2

Composition-Temperature Diagram for the System NaO_2–Na_2O

Temperature (°C)	Composition	Temperature (°C)	Composition
100	$Na_2O_{3.89}$	294	$Na_2O_{2.69}$
122	$Na_2O_{3.87}$	304	$Na_2O_{2.69}$
143	$Na_2O_{3.84}$	354	$Na_2O_{2.69}$
152	$Na_2O_{3.90}$	386	$Na_2O_{1.98}$
164	$Na_2P_{3.97}$	408	$Na_2O_{1.97}$
190	$Na_2O_{3.94}$	432	$Na_2O_{1.88}$
208	$Na_2O_{3.79}$	452	$Na_2O_{1.94}$
221	$Na_2O_{3.78}$	488	$Na_2O_{1.88}$
230	$Na_2O_{3.79}$	510	$Na_2O_{1.86}$
244	$Na_2O_{3.68}$	526	$Na_2O_{1.78}$
254	$Na_2O_{3.69}$	546	$Na_2O_{1.78}$
262	$Na_2O_{3.72}$	554	$Na_2O_{1.71}$
266	$Na_2O_{3.80}$	558	$Na_2O_{1.69}$
272	$Na_2O_{3.64}$	568	$Na_2O_{1.88}$
274	$Na_2O_{2.44}$	572	$Na_2O_{1.58}$ + silicate
280	$Na_2O_{2.53}$	583	$Na_2O_{1.58}$ + silicate
284	$Na_2O_{2.68}$	592	Sodium silicate

A comparative examination of all our results enabled us to construct the composition-temperature diagram for the system NaO_2–Na_2O, which we give in Fig. 6. The corresponding numerical data are given in Table 2.

This is not an equilibrium diagram, but corresponds to a rate of heating of 5.5-6° per minute. The region of the diagram corresponding to solid solutions is shaded.

In the section a-b (100-250°) there is a continuous series of solid solutions having a limiting composition corresponding to the formula $Na_2O_{3.69}$ and having the lattice of NaO_2. As already stated, the X-ray powder photographs showed displacement of the interference lines (see Table 1).

At 250° the limiting solid solution begins to decompose vigorously to give Na_2O_2. This begins to decompose slightly to sodium oxide already in the solid state at temperatures from 380° to 510° (section d-f). At 510° sodium peroxide melts and its slow decomposition continues also in the liquid state up to 545°. At this temperature vigorous decomposition of residual liquid peroxide occurs with formation of solid Na_2O. Between 510° and 545° there is a heterogeneous region on the diagram corresponding to mixture of sodium peroxide melt and solid sodium oxide.

SUMMARY

1. It was shown that NaO_2 begins to decompose at about 120° in an atmosphere of dry oxygen and at about 80-90° in an atmosphere of dry CO_2-free air. In the course of its thermal decomposition it gives a continuous series of solid solutions up to the limiting composition of $Na_2O_{3.69}$.

2. $Na_2O_{3.69}$ decomposes vigorously and endothermically into Na_2O_2 at about 250° in oxygen and about 215° in dry CO_2-free air.

3. Slight decomposition of Na_2O_2 is observed in the solid state from 300° upward. At 510° Na_2O_2 melts. At 545° there is vigorous decomposition of residual liquid peroxide with formation of solid Na_2O. Between 510° and 545° there is a heterogeneous region on the diagram corresponding to Na_2O_2 melt and solid Na_2O. The latter reacts exothermically with the glass or stainless steel of the vessel, but does not react with nickel.

4. The existence of the following phases of constant composition was established for the system NaO_2–Na_2O: three modifications of NaO_2 having transition temperatures of −80° and −45°, Na_2O_2, and Na_2O. Phases of variable composition were found ranging from Na_2O_2 to $Na_2O_{2.25}$. We were unable to establish the formation of the compound Na_2O_3 under our conditions.

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SCISSION OF THE CARBON – CARBON BOND IN COMPOUNDS CONTAINING THE TRIPHENYLMETHYL GROUP

A. N. Nesmeyanov, V. F. Lavrushin, T. M. Shmaeva, and E. G. Perevalova

In a study of compounds of the type $[(CH_3)_2NC_6H_4]_2C-CH_2-Y=X$ it has been shown that the bond attaching tris(p-dimethylaminophenyl)methyl with the rest of the molecule is very labile and is readily broken by the action of carboxylic acids and magnesium bromide with formation of Crystal violet in the case of 3,3,3-tris(p-dimethylaminophenyl)propionaldehyde, 3,3,3-tris(p-dimethylaminophenyl)-2-methylpropionaldehyde, 5,5,5-tris(p-dimethylaminophenyl)-2-pentenal, and 1,1,1-tris(p-dimethylaminophenyl)-2-nitroethane, i.e. compounds in which the $>C-CH_2-$ bond is conjugated with a C=O or N=O bond. In the case of allyltris(p-dimethylaminophenyl)methane and tris(p-dimethylaminophenyl)propylmethane, no Crystal violet could be isolated [1, 2].

In the present investigation we have made a spectrophotometric study of solutions of 3,3,3-tris(p-dimethylaminophenyl)propionaldehyde, allyltris(p-dimethylaminophenyl)methane, and tris(p-dimethylaminophenyl)propylmethane after treatment with acetic, chloroacetic, and trichloroacetic acids, and we have also measured the absorption spectra of these compounds in some polar solvents (acetic anhydride, bromobenzene, and nitrobenzene).

As shown previously [1], when boiled with acetic acid, 3,3,3-tris(p-dimethylaminophenyl)propionaldehyde is completely converted into Crystal violet. It was shown in the present investigation that chloroacetic and trichloroacetic acids act similarly.

3,3,3-Tris(p-dimethylaminophenyl)propionaldehyde was heated with chloroacetic and trichloroacetic acids at 100°. The resulting solutions were diluted with ethanol for absorption spectrum measurements. When the aldehyde was heated with acetic and chloroacetic acids there was an intense bluish-violet coloration, but when it was heated with trichloroacetic acid the solution became orange-yellow, but turned bluish-violet when diluted with ethanol.

The absorption curves for these bluish-violet solutions were almost identical with the curve for Crystal violet, as can be seen from Fig. 1. It must be pointed out that, even in the case of trichloroacetic acid (when the auxochromes are partially excluded from conjugation), acidolysis occurs. Fig. 2 gives the absorption curves for solutions of the aldehyde in acetic anhydride, bromobenzene, and nitrobenzene. As they are all completely identical with the curve for Crystal violet, we consider that, under the influence of polar solvents, dissociation occurs with formation of the Crystal violet cation.

It was of great interest to examine the behavior of allyltris(p-dimethylaminophenyl)methane and tris(p-dimethylaminophenyl)propylmethane, for which no scission products were isolated. The absorption curves for allyltris(p-dimethylaminophenyl)methane given in Fig. 3 show that this compound is also partially split by treatment with acetic and trichloroacetic acids with formation of Crystal violet. The absorption curves for solutions in acetic anhydride and bromobenzene are similar.

Tris(p-dimethylaminophenyl)propylmethane behaved differently. Even when this substance was boiled in polar solvents for a long time, no coloration appeared; this result indicates absence of scission of the molecule. Hence, in tris(p-dimethylaminophenyl)propylmethane the bond formed by tris(p-dimethylaminophenyl)methyl with propyl is less labile than the corresponding bond in allyltris(p-dimethylaminophenyl)methane and the aldehyde studied. In our opinion this results from the absence in the propyl group of a double bond conjugated with the methane C–C linkage.

The absorption curves of ethanol solutions of tris(p-dimethylaminophenyl)propylmethane that had been treated with acetic and trichloroacetic acids were found to be different in character, as can be seen from Fig. 4. It is possible that in this case the linkage to one of the benzene rings is broken, as observed by one of us in a series of arylmethanes [3-5].

Fig. 1. Absorption curves for solutions of 3.3.3-tris(p-dimethylaminophenyl)propionaldehyde: 1) in CH_3COOH; 2) in $CH_2ClCOOH$ + C_2H_5OH; 3) in CCl_3COOH + C_2H_5OH; 4) aqueous Crystal violet in H_2O.

Fig. 2. Absorption curves for solutions of 3.3.3-tris(p-dimethylaminophenyl)propionaldehyde: 1) in $(CH_3CO)_2O$; 2) in C_6H_5Br; 3) in $C_6H_5NO_2$; 4) aqueous Crystal violet in H_2O.

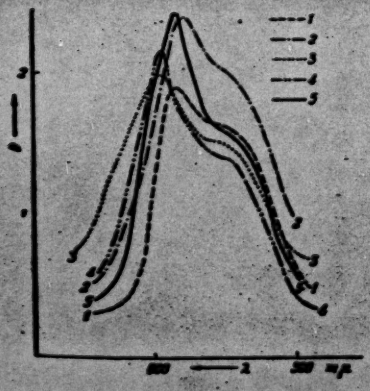


Fig. 3. Absorption curves for solutions of allylidene-(p-dimethylaminophenyl)methane: 1) in CH_3COOH; 2) in CCl_3COOH + C_2H_5OH; 3) in $(CH_3CO)_2O$; 4) in C_6H_5Br; 5) aqueous Crystal violet in H_2O.

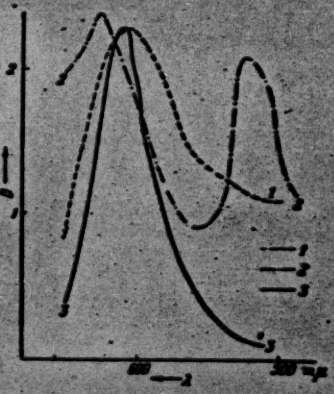


Fig. 4. Absorption curves for solutions of tris(p-dimethylaminophenyl)propylmethane: 1) in CH_3COOH; 2) in $CH_2ClCOOH$ + C_2H_5OH; 3) Malachite green in C_2H_5OH.

The results we have given present a qualitative picture of the behavior of the compounds under investigation in their interactions with acids and when dissolved in polar solvents. In order to characterize these processes quantitatively, we have carried out experiments to determine the extent to which the molecules of these compounds are broken down under various conditions.

EXPERIMENTAL

An exactly weighed sample of the substance to be investigated was dissolved in a suitable solvent, and the solution was heated or was maintained at room temperature. For optical-density measurements, these solutions were diluted with ethanol in the case of acetic, chloroacetic, and trichloroacetic acids, or with the solvent used in the preparation of the original solution — in the other cases. The extent to which the molecules of the compounds were broken down (α) was calculated from the value of the molar extinction coefficient determined for a wavelength in the region of the absorption maximum of the principal band of the compound. The results are given in the table.

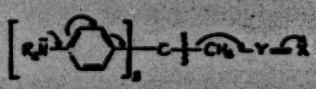
TABLE

Substance	Solvent	Temperature (°C)	Time (hours)	α (%)
CrV—CH_2—C(=O)H	CH_3COOH	100	3.0	100.0
Also	Also	20	240.0	8.2
"	"	20	1560.0	26.2
"	$CH_2ClCOOH$	100	1.0	7.4
"	CCl_3COOH	100	2.5	3.7
"	$(CH_3CO)_2O$	100	7.0	4.2
"	Also	20	72.0	1.3
"	C_6H_5Br	100	13.5	5.9
"	Also	100	20.0	15.8
"	"	20	2160.0	0.6
"	$C_6H_5NO_2$	100	3.0	3.2
"	Also	100	13.0	10.8
"	"	100	20.0	19.8
"	"	20	120.0	1.0
"	"	20	1620.0	4.1
CrV—CH_2—CH = CH_2	CH_3COOH	100	7.0	8.1
Also	CCl_3COOH	200	2 min.	12.8
"	$(CH_3CO)_2O$	100	7.0	3.3
"	Also	20	72.8	0.2
"	C_6H_5Br	100	13.5	0.5
CrV—CH_2—CH_2—CH_3	CH_3COOH	100	2.5	0.8
Also	Also	100	4.3	1.2
"	$CH_2ClCOOH$	100	1.0	0.1

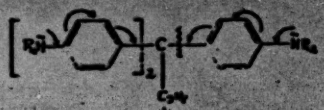
* CrV = $[(CH_3)_2N{-}C_6H_4]_3{-}C{-}$.

The data given in the table on the degree of acidolysis or dissociation of the compounds studied show that the C—CH_2 bond is most mobile in the aldehyde, less mobile in allyltris(p-dimethylaminophenyl)methane, and only very slightly mobile in tris(p-dimethylaminophenyl)propylmethane.

It is probable that, when there is a unified conjugated chain, scission of the C—C bond will occur between the methane carbon and the electron-accepting substituent.



When no such conjugated chain is present, the scission must occur at the bond with the electron-donating substituent:



This conclusion requires further experimental confirmation.

SUMMARY

1. Absorption spectra were measured for 3,3,3-tris(p-dimethylaminophenyl)propionaldehyde, allylbis(p-dimethylaminophenyl)methane, and tris(p-dimethylaminophenyl)propylmethane as solutions in polar solvents and after interaction with acetic, chloroacetic, and trichloroacetic acids.

2. On the basis of the photospectrometric data it was shown that scission of a C—C bond occurs in the first two compounds under the action of acids and polar solvents, but in the third only under the action of acids.

3. It was shown how the scission of the C—C bond depends on the character of the conjugation in the molecules of the compounds investigated.

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ALLYL REARRANGEMENT IN SOME SUBSTITUTED POLYHALOALLYL ALCOHOLS

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Allyl anionotropic rearrangement of substituted allyl alcohols containing halogen at the double bond has been studied in detail only for the monochloro derivatives $RR'C(OH)CH=CHCl$, which give α,β-unsaturated aldehydes by rearrangement [1-3]. As regards dichloro derivatives of allyl alcohols, it has been noted that, for example, 1,1-dichloro-3-methyl-1-nonen-4-yn -3-ol cannot undergo rearrangement into the corresponding unsaturated acid [2]. 1,1,3-Trichloropropene [4] and 1,1,3-trichloro-2-methylpropene [5], which contain the system $ClC-C=CCl_2$, are also found to be incapable of the allyl rearrangement. It was of interest to make a more detailed investigation of the possibility of allyl rearrangement of polyhaloallyl alcohols (and their ethers) in accordance with the following schemes:

$$RR'C(OH)CH=CX_2 \longrightarrow [RR'C=CHCX_2OH] \longrightarrow RR'C=CH-COOH;$$
(I)

$$RR'C(OH)CX=CHX \longrightarrow [RR'C=CX-CHXOH] \longrightarrow RR'C=CX-CHO;$$
(II)

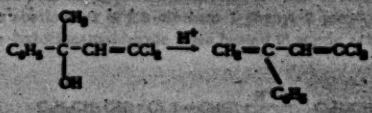
$$RR'C(OH)CX=CX_2 \longrightarrow [RR'C=CX-CX_2OH] \longrightarrow RR'C=CX-COOH,$$
(III)

in which X is a halogen.

Compounds of formula (I) in which the substituents are alkyl groups were found to be incapable of rearrangement, even under severe conditions. When 1,1-dichloro-1-hepten-3-ol was heated for a long time with 10% sulfuric acid in aqueous alcohol or aqueous dioxane, it was recovered unchanged, and its ethyl ether was recovered similarly when it was heated in acetic acid solution. In an acid medium 4,4-dichloro-2-methyl-3-buten-2-ol readily eliminated water with formation of 1,1-dichloro-3-methyl-1,3-butadiene, but its methyl ether, heated with 10% sulfuric acid in aqueous-alcoholic solution, was recovered unchanged. Compounds of formula (I) in which R is aryl and R' is hydrogen are readily rearranged in an acid medium into 3-arylacrylic acids:

$$ArCH(OH)-CH=CCl_2 \xrightarrow[H_2O]{H^+} ArCH=CH-COOH$$
(or an acetic acid)

The reaction was carried out by heating an acetic acid solution of the aryl derivative with hydrochloric acid. The aryl substituents studied were phenyl, p-tolyl, 1-naphthyl, and p-chlorophenyl*. However, 4,4-dichloro-2-phenyl-3-buten-2-ol did not undergo rearrangement either under these conditions or when treated with 10% sulfuric acid in aqueous-alcoholic solution; only elimination of water occurred with formation of 1,1-dichloro-3-phenyl-1,3-butadiene:



* The rearrangement of some of these compounds has been published previously by the author in collaboration with Nesmeyanov and Freidlina [6].

When heated, this product dimerized and lost a molecule of hydrogen chloride, giving a compound of composition $C_{10}H_5Cl_5$.

The presence of a negative substituent in compounds of formula (I) inhibits anionotropic rearrangement even when the displacement of the double bond permits the formation of a conjugated system. Thus, when 4, -dichloro-2-ethoxy (or hydroxy)-3-butenenitrile was heated in an acid medium, no anionotropic allyl rearrangement occurred with formation of fumaric acid, but only hydrolysis of the nitrile group to carboxyl occurred. On the other hand, 4,4-dichloro-2-ethoxy-3-butenenitrile readily underwent prototropic allyl rearrangement under the action of triethylamine with formation of 4,4-dichloro-2-ethoxycrotonitrile [7]. When heated in dilute hydrochloric acid, this product underwent an interesting conversion into 3-chloroacrylic acid:

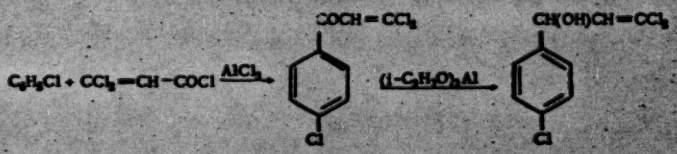
$$CCl_2{=}CH{-}\underset{\displaystyle OC_2H_5}{\underset{|}{CH}}{-}CN \xrightarrow{(C_2H_5)_3N} CHCl_2{-}CH{=}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{-}CN \xrightarrow[H_2O]{H^+} [CHCl_2CH_2COCN] \rightarrow$$

$$\rightarrow CHCl{=}CH{-}COOH + HCN$$

The synthesis of compounds of formula (I) was carried out as follows: 4,4-dichloro-2-methyl-3-buten-2-ol was prepared by the action of methylmagnesium iodide on 4,4-dichloro-3-buten-2-one; 1,1-dichloro-1-hepten-3-ol, 1,1-dichloro-3-ethoxy-1-heptene, 1-aryl-3,3-dichloro-2-propen-1-ols, and 3-aryl-1,1-dichloro-3-ethoxypropenes were prepared by the action of the corresponding organomagnesium compounds on 3,3-dichloroacrolein or 1,1,3-trichloro-3-ethoxypropene:

$$RMgX + CCl_2{=}CH{-}\underset{\displaystyle OC_2H_5}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{CH}}}} \longrightarrow R{-}\underset{\displaystyle OC_2H_5}{\underset{|}{CH}}{-}CH{=}CCl_2$$

3,3-Dichloro-1-p-chlorophenyl-2-propen-1-ol was prepared as indicated:



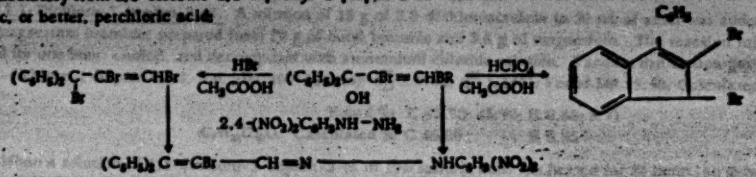
The 3,3-dichloroacrylic acid required for this reaction was prepared by the oxidation of 3,3-dichloroacrolein with chromic anhydride in acetone solution. 4,4-Dichloro-2-ethoxy-3-butenenitrile was prepared by the action of cuprous cyanide on 1,1,3-trichloro-3-ethoxypropene.

With respect to allyl rearrangement, compounds of formula (II) behaved similarly to the compounds (I). When there were alkyl substituents rearrangement did not occur, even under severe conditions. When treated with 10% sulfuric acid in aqueous-alcoholic solution at room temperature, 1,2-dibromo-1-hexen-3-ol, 1,2-dibromo- and 1,2-dichloro-3-methyl-1-penten-3-ols, and 1-(1,2-dibromovinyl)cyclohexanol were unaffected (recovered unchanged), and when heat was applied elimination of water or resinification resulted. 2,3-Dichloro-1-phenyl-2-propen-1-ol and the acetic ester of 2,3-dibromo-1-phenyl-2-propen-1-ol readily underwent rearrangement into the corresponding α-halocinnamaldehyde when heated in acetic acid solution in presence of hydrochloric acid:

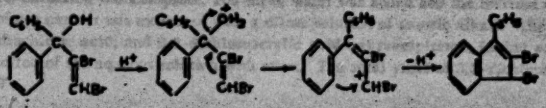
$$C_6H_5CH(OH){-}CCl{=}CHCl \xrightarrow[H_2O]{H^+} C_6H_5CH{=}CCl{-}CHO$$

2,4 Dibromo-2-phenyl-3-buten-2-ol, like 4,4-dichloro-2-phenyl-3-buten-2-ol, does not undergo rearrangement in an acid medium, but eliminates water. It is interesting to note that 4-chloro-2-phenyl-3-buten-2-ol is rearranged into the corresponding aldehyde [3]. The behavior of 2,3-dibromo-1,1-diphenyl-2-propen-1-ol in an acid medium possessed several peculiarities: when it was treated in acetic acid solution with hydrochloric or hydrobromic acid,

the product first formed was 1,2-dibromo-3-chloro- or 1,2,3 tribromo 3,3 diphenylpropene, respectively, which, when heated in 90% acetic acid solution, was converted not into 2-bromo-3,3-diphenylacrolein, but into 1,2-dibromo-3-phenylindene, although both of these trihalo compounds, and also 2,3-dibromo-1,1-diphenyl-2-propen-1-ol, gave the 2,4-dinitrophenylhydrazone of 2-bromo-3,3-diphenylacrolein when treated with 2,4-dinitrophenylhydrazine in alcoholic solution in presence of sulfuric acid. 1,2-Dibromo-3-phenylindene was formed immediately from 2,3-dibromo-1,1-diphenyl-2-propen-1-ol when this was treated in acetic acid solution with sulfuric, or better, perchloric acid:



The formation of 1,2-dibromo-3-phenylindene can be represented as follows:



The structure of 1,2-dibromo-3-phenylindene follows from its conversion into o-benzoylbenzoic acid by permanganate oxidation. Compounds of formula (II) were prepared by addition of bromine to the corresponding acetylenic alcohols.

The possibility of rearrangement in the system $RR'C(OH)CX=CX_2$ was investigated for the case of 2,3,3-trichloro-1-phenyl-2-propen-1-ol. When this substance was heated in acetic acid solution in presence of hydrochloric acid, it was converted into α-chlorocinnamic acid:

$$C_6H_5CH(OH)-CCl=CCl_2 \xrightarrow[H_2O]{H^+} C_6H_5CH=CCl-COOH$$

This rearrangement went much less readily than that of 3,3-dichloro-1-phenyl-2-propen-1-ol: 75% conversion of the 2,3,3-trichloro compound into α-chlorocinnamic acid required heating for 25 hours, whereas the 3,3-dichloro compound was converted completely into cinnamic acid in 30-40 minutes. 2,3,3-Trichloro-1-phenyl-2-propen-1-ol, was prepared by the reduction of 2,3,3-trichloroacrylophenone with aluminum isopropoxide.

EXPERIMENTAL

4,4-Dichloro-2-methyl-3-buten-2-ol. 4,4-Dichloro-3-buten-2-one was prepared from 1,1-dichloroethylene and acetyl chloride [2]. It was allowed to stand, when hydrogen chloride was eliminated and a solid was found; m.p. 66-67° (from petroleum ether-benzene mixture); b.p. 173-174° (8 mm).

Found %: C 46.47; 46.70; H 2.67; 2.86; Cl 34.74; 34.96

$C_5H_6Cl_2O_2$. Calculated %: C 46.62; H 2.92; Cl 34.63

Found: M 202.5 (cryoscopically in benzene)

Calculated: M 205

4,4-Dichloro-3-buten-2-one (28 g) was added to a stirred ethereal solution of methylmagnesium iodide (prepared from 32 g of methyl iodide and 5.6 g of magnesium in 70 ml of ether). The reaction mixture was heated for one hour, cooled, and decomposed with ammonium chloride solution. The ethereal solution was dried with potassium carbonate. Vacuum distillation yielded 22.4 g (78%) of 4,4-dichloro-2-methyl-3-buten-2-ol, b.p. 60-61° (20 mm); n_D^{25} 1.4780; d_4^{20} 1.2220; Found MR 35.91; Calculated MR 36.08.

Found %: C 38.92; 38.86; H 7.41; 7.38

$C_5H_8Cl_2O$. Calculated %: C 38.71; H 7.89

When the 4,4-dichloro-2-methyl-3-buten-1-ol was allowed to stand, water was eliminated. It was allowed to stand in an aqueous-alcoholic solution of sulfuric acid (10%), and on the next day an oil had separated, which was extracted with ether. Distillation gave 1,1-dichloro-3-methyl-1,3-butadiene, b.p. 34-35° (11 mm) and n_D^{20} 1.5030. No senecioic acid was detected.

1,1-Dichloro-1-hepten-3-ol. A solution of 15 g of 2,3-dichloroacrolein in 30 ml of ether was added to butylmagnesium bromide, prepared from 22 g of butyl bromide and 3.6 g of magnesium. The reaction mixture was heated for one hour, cooled, and decomposed with ammonium chloride solution. Vacuum distillation gave 17.8 g of 1,1-dichloro-1-hepten-3-ol, b.p. 103-104° (8 mm); n_D^{23} 1.4791; d_4^{20} 1.1431; Found MR 45.40; Calculated MR 45.22.

Found %: C 45.72; 45.70; H 6.68; 6.71
$C_7H_{12}Cl_2O$. Calculated %: C 45.90 H 6.55

When a solution of 1,1-dichloro-1-hepten-3-ol in 10% sulfuric acid was heated for 24 hours, no 2-heptenoic acid was obtained, the original compound being recovered unchanged.

3,3-Dichloroacrylic Acid. A solution of 25 g of chromic anhydride in a mixture of 40 g of concentrated sulfuric acid and 90 ml of water was added gradually to a cooled solution of 37.5 g of 2,3-dichloroacrolein in 120 ml of acetone. When the oxidation was complete, 100 ml of water was added and the mixture was extracted with chloroform. The chloroform extract was extracted with a dilute solution of caustic alkali. The alkaline solution was acidified with hydrochloric acid, and 3,3-dichloroacrylic acid was precipitated; further amounts of the acid were obtained by extraction of the aqueous solution with ether. The total yield of 3,3-dichloroacrylic acid was 24.8 g (59%); m.p. 76-77°.

3,3,4'-Trichloroacrylophenone. 3,3-Dichloroacryloyl chloride was prepared in 85% yield by heating 3,3-dichloroacrylic acid with excess of thionyl chloride; it boiled at 143-144°. Aluminum chloride (7 g) was added gradually to a stirred mixture of 8.5 g of 3,3-dichloroacryloyl chloride and 12 g of chlorobenzene, and the mixture was heated for 15-20 minutes at 70-80°. The mixture was cooled and decomposed with ice water. Vacuum distillation gave 10.1 g of 3,3,4'-trichloroacrylophenone, b.p. 168-169° (8 mm) and m.p. 51-52° (from petroleum ether).

Found %: C 45.65; 45.78; H 2.02; 2.04
$C_9H_5Cl_3O$. Calculated %: C 45.88; H 2.12

3,3-Dichloro-1-p-chlorophenyl-2-propen-1-ol. A mixture of 10 g of 3,3,4'-trichloroacrylophenone, 12 g of aluminum isopropoxide, and 80 ml of isopropyl alcohol was heated, acetone being allowed to distil off. When the reduction was complete, the mixture was carefully decomposed with dilute sulfuric acid. The reaction product was extracted with chloroform and dried with potassium carbonate. Vacuum distillation gave 8.1 g of 3,3-dichloro-1-p-chlorophenyl-2-propen-1-ol, b.p. 142-143° (3 mm); n_D^{20} 1.5730; d_4^{20} 1.3998; Found MR 55.90; Calculated MR 55.72.

Found %: C 45.25; 45.38; H 2.90; 2.81
$C_9H_7Cl_3O$. Calculated %: C 45.47; H 2.94

p-Chlorocinnamic Acid. Heating of a solution of 3,3-dichloro-1-p-chlorophenyl-2-propen-1-ol in acetic acid containing hydrochloric acid for one hour gave a 92% yield of p-chlorocinnamic acid, m.p. 244-245° (from glacial acetic acid); the literature [6] gives m.p. 245°.

4,4-Dichloro-2-phenyl-3-buten-2-ol. A solution of 13 g of 4,4-dichloro-3-buten-2-one in 15 ml of ether was added to a cooled stirred ethereal solution of phenylmagnesium bromide (from 17 g of bromobenzene and 2.7 g of magnesium in 40 ml of ether). The reaction mixture was heated for 20 minutes, cooled, and decomposed, with ammonium chloride solution. The ethereal solution was dried with potassium carbonate. Vacuum distillation in a current of nitrogen gave 14.8 g (72%) of 4,4-dichloro-2-phenyl-3-buten-2-ol, b.p. 186-187° (2 mm); n_D^{20} 1.5574; d_4^{20} 1.2567; Found MR 55.65; Calculated MR 55.67.

Found %: C 55.11; 55.32; H 4.81; 4.72
$C_{10}H_{10}Cl_2O$. Calculated %: C 55.30; H 4.60

When a solution of 12 g of 4,4-dichloro-2-phenyl-3-buten-2-ol in a mixture of 175 ml of glacial acetic acid, 100 ml of water, and 12 ml of concentrated sulfuric acid was allowed to stand overnight, an oil separated. After five days the mixture was diluted with water, the oil was extracted with chloroform, and the chloroform extract was washed with sodium carbonate solution. Vacuum distillation gave 10.1 g (92%) of 1,1-dichloro-3-phenyl-1,3-butadiene, b.p. 86-87° (1.5 mm); n_D^{20} 1.5929; d_4^{20} 1.2048.

Found %: C 60.48; 60.52; H 4.15; 4.21
$C_{10}H_9Cl_3$. Calculated %: C 60.30; H 4.02

No β-methylcinnamic acid was found. When 1,1-dichloro-3-phenyl-1,3-butadiene was heated at 130-150°, hydrogen chloride was evolved and a compound of composition $C_{20}H_{16}Cl_2$ was obtained in good yield; it had b.p. 208-210° (2 mm) and m.p. 132-133° (from a mixture of petroleum ether and benzene).

Found %: C 66.82; 66.82; H 4.32; 4.21
$C_{20}H_{16}Cl_2$. Calculated %: C 66.40; H 4.15

Found: M 362 (cryoscopically in benzene)
Calculated: M 361.4

4,4-Dichloro-2-ethoxy-3-butenenitrile. A mixture of 62 g of 1,1,3-trichloro-3-ethoxypropene and 40 g of cuprous cyanide was heated with stirring at 130-160° for four hours. The reaction mixture was cooled, chloroform was added, and the whole was transferred to a Wurtz flask. Solvent was removed under somewhat reduced pressure, and the nitrile was then distilled off from the copper salts. Redistillation yielded 51 g of 4,4-dichloro-2-ethoxy-3-butenenitrile, b.p. 84-85° (8 mm); n_D^{20} 1.4642; d_4^{20} 1.2160; Found MR 40.90; Calculated MR 40.64.

Found %: N 7.56; 7.68
$C_6H_7Cl_2NO$. Calculated %: N 7.77

In a similar way, 3-butoxy-1,1,3-trichloropropene gave 2-butoxy-1,1,3-trichloropropene, b.p. 102-103° (5 mm); n_D^{20} 1.4635; d_4^{20} 1.1443; Found MR 50.11; Calculated MR 49.87.

Found %: N 6.85; 6.92
$C_9H_{13}Cl_3NO$. Calculated %: N 6.73

4,4-Dichloro-2-ethoxy-3-butenoic Acid. A solution of 20 g of 4,4-dichloro-2-ethoxy-3-butenenitrile in a mixture of 60 ml of acetic acid, 30 ml of concentrated hydrochloric acid, and 30 ml of water was boiled for ten hours. Acetic acid was then distilled off under reduced pressure. A little water was added to the residue, and the oil that separated was extracted with chloroform. The product (20 g) was 4,4-dichloro-2-ethoxy-3-butenoic acid, b.p. 114-115° (2 mm); n_D^{20} 1.4899; d_4^{20} 1.3445; Found MR 42.71; Calculated MR 42.35.

Found %: C 39.52; 39.54; H 4.41; 4.56
$C_6H_8Cl_2O_3$. Calculated %: C 39.34; H 4.37

No fumaric acid could be found in the hydrolysis products.

4,4-Dichloro-2-ethoxycrotononitrile. A few drops of triethylamine were added to 20 g of 4,4-dichloro-2-ethoxy-3-butenenitrile. The mixture became appreciably warm. On the next day the reaction product was vacuum-distilled, the product being 19 g of 4,4-dichloro-2-ethoxycrotononitrile, b.p. 86° (10 mm); n_4^{20} 1.4797; d_4^{20} 1.2074. A second treatment with triethylamine did not affect the constants.

Found %: N 7.62; 7.73
$C_6H_7Cl_2NO$. Calculated %: N 7.77

In a similar way 2-butoxy-4,4-dichloro-3-butenenitrile was isomerized into 2-butoxy-4,4-dichlorocrotononitrile, b.p. 96-97° (4 mm); n_D^{20} 1.4760; d_4^{20} 1.1347

Found %: N 6.72; 6.68
$C_9H_{13}Cl_2NO$. Calculated %: N 6.73

3-Chloroacrylic Acid. A mixture of 28 g of 4,4-dichloro-2-ethoxycrotononitrile, 150 ml of water, and 5 ml of concentrated hydrochloric acid was refluxed for three hours. Hydrogen cyanide was evolved. After being cooled, the solution was extracted with ether. The product (12.2 g) was 3-chloroacrylic acid, m.p. 85-95° (from petroleum ether); the literature [9] gives m.p. 85-86°.

1,2-Dibromo-3-methyl-1-penten-3-ol. This was prepared in almost quantitative yield by treatment of an illuminated solution of 3-methyl-1-penten-3-ol in carbon tetrachloride with bromine at 35-40°; it had b.p. 98-99° (7 mm); n_D^{20} 1.5380; d_4^{20} 1.7417; Found MR 64.34; Calculated MR 64.80.

Found %: C 27.82; 28.01; H 3.81; 3.71
$C_6H_{10}Br_2O$. Calculated %: C 27.90; H 3.87

After it had been allowed to stand in aqueous-alcoholic 10% sulfuric acid for ten days at room temperature, it was recovered from the mixture unchanged.

A solution of 40 g of 1,2-dibromo-3-methyl-1-penten-3-ol in a mixture of 80 ml of glacial acetic acid, 7 ml of concentrated hydrochloric acid, and 10 ml of water was heated for two hours. An oil separated, and when the reaction mixture was cool it was diluted with water and extracted with chloroform. Vacuum fractionation gave two fractions: Fraction I, b.p. 43-45° (2 mm) and n_D^{20} 1.5340-1.5417, 14.2 g; and Fraction II, b.p. 80-86° (2 mm) and n_D 1.5590, 9.8 g. Fraction II was found to be 1,2-dibromo-3-methyl-1,3-pentadiene (or its isomer), b.p. 88-89° (7 mm); n_D^{20} 1.5641; d_4^{20} 1.6863.

Found %: C 30.55; 30.25; H 3.37; 3.45
$C_6H_8Br_2$. Calculated %: C 30.00 H 3.33

Fraction I was a mixture containing a small amount of carbonyl compound, since it formed a 2,4-dinitrophenylhydrazone, m. p. 194-197° (from glacial acetic acid), which did not contain halogen.

1,2-Dibromo-1-hexen-3-ol. Treatment of an illuminated solution of 20 g of 1-hexyn-3-ol in 50 ml of carbon tetrachloride with bromine at 30° gave 26.3 g of 1,2-dibromo-1-hexen-3-ol, b.p. 78-79° (1 mm); n_D^{20} 1.5390; d_4^{20} 1.7414; Found MR 64.36; Calculated MR 64.50.

Found %: C 28.11; 28.08; H 3.92; 3.98
$C_6H_{10}Br_2O$. Calculated %: C 27.90; H 3.87

After the 1,2-dibromo-1-hexen-3-ol had been allowed to stand for a week in aqueous alcoholic 10% sulfuric acid, the whole of it was recovered unchanged b.p. 112-113°(8 mm). No aldehyde was detected.

1-(1,2-Dibromovinyl)cyclohexanol. This was prepared in almost quantitative yield by treatment of an illuminated solution of 1-ethynylcyclohexanol with bromine at 45-50°; b.p. 128-129° (5 mm); m.p. 73-74° (from aqueous alcohol).

Found %: C 33.66; 33.58; H 4.17; 4.12
$C_8H_{12}OBr_2$. Calculated %: C 33.80; H 4.23

When a solution of 37 g of 1-(1,2-dibromovinyl)cyclohexanol in a mixture of 80 ml of acetic acid, 5 ml of concentrated hydrochloric acid, and 10 ml of water was heated for one hour, an oil separated. The reaction mixture was cooled, diluted with water, and extracted with chloroform. Vacuum fractionation gave 12.3 g of a fraction having b.p. 87-90° (8 mm), n_D^{20} 1.5560; d_4^{20} 1.2915, and containing a small amount of a carbonyl compound, since a 2,4-dinitrophenylhydrazone (m. p. 240-241° from glacial acetic acid) was obtained; the carbonyl compound did not contain halogen.

Acetic Ester of 2,3-Dibromo-1-phenyl-2-propen-1-ol. Addition of 18 g of bromine to 17 g of the acetic ester of 1-phenyl-2-propyn-1-ol in carbon tetrachloride solution gave 28 g of the acetic ester of 2,3-dibromo-1-phenyl-2-propen-1-ol, b.p. 139-140° (1.5 mm); n_D^{20} 1.5752; d_4^{20} 1.6705; Found MR 66.14; Calculated MR 66.01.

Found %: C 39.67; 39.56; H 3.06; 3.13
$C_{11}H_{10}Br_2O_2$. Calculated %: C 39.52; H 2.99

The addition of bromine to 1-phenyl-2-propyn-1-ol itself did not proceed altogether smoothly, for water and hydrogen bromide separated in the reaction.

α-Bromocinnamaldehyde. A solution of 10 g of the acetic ester of 2,3-dibromo-1-phenyl-2-propen-1-ol in a mixture of 40 ml of acetic acid, 3 ml of concentrated hydrochloric acid, and 5 ml of water was heated for one hour. Dilution of the cooled reaction mixture with water gave a precipitate of 5.8 g (95%) of α-bromocinnamaldehyde, m.p. 70-71° (from alcohol); oxime, m.p. 135-136°.

2,3-Dichloro-1-phenyl-2-propen-1-ol. This was prepared in low yield by addition of chlorine to 1-phenyl-2-propyn-1-ol in carbon tetrachloride solution. It had b.p. 105-106° (3 mm); n_D^{20} 1.5723; d_4^{20} 1.3226; Found MR 50.56; Calculated MR 50.95.

Found %: C 52.95; 52.98; H 3.69; 3.76
$C_9H_8Cl_2O$. Calculated %: C 52.30; H 3.94

α Chlorocinnamaldehyde. A solution of 5 g of 2,3-dichloro-1-phenyl-2-propen-1-ol in acetic acid containing hydrochloric acid was heated for one hour. The product (3.2 g) was α-chlorocinnamaldehyde, b.p. 122-123° (9 mm); oxime, m.p. 158-159°.

3,1-Dibromo-2-phenyl-3-buten-2-ol. This was prepared in almost quantitative yield by treating an illuminated solution of 2-phenyl-3-butyn-2-ol in carbon tetrachloride with bromine at 45-55°. It had b.p. 134-135° (2 mm); n_D^{30} 1.6061; d_4^{20} 1.7217; Found MR 61.37; Calculated MR 61.37

Found %: C 39.01; 39.08; H 3.12; 3.09
$C_{10}H_{10}Br_2O$. Calculated %: C 39.21; H 3.26

When it was heated in acetic acid solution in presence of hydrochloric acid, the corresponding aldehyde was not formed.

2,3-Dibromo-1,1-diphenyl-2-propen-1-ol. 1,1-Diphenyl-2-propyn-1-ol was prepared by the action of sodium acetylide on benzophenone in liquid ammonia. When treated in alcoholic solution with 2,4-dinitrophenylhydrazine in presence of sulfuric acid, 1,1-diphenyl-2-propyn-1-ol was converted almost quantitatively into the 2,4-dinitrophenylhydrazone of 3,3-diphenylacrolein, m.p. 196-197° (from acetic acid).

A solution of 4 g of bromine in 10 ml of carbon tetrachloride was added to an illuminated solution of 5 g of 1,1-diphenyl-2-propyn-1-ol in 30 ml of carbon tetrachloride. The solution was boiled for one hour under illumination, and was then cooled and washed with sodium carbonate solution. A solid remained after removal of solvent. The yield of 2,3-dibromo-1,1-diphenyl-2-propen-1-ol was 8 g; m.p. 112-113° (from a mixture of benzene and petroleum ether).

Found %: C 49.39; 49.30; H 3.29; 3.40
$C_{15}H_{12}Br_2O$. Calculated %: C 49.20; H 3.28

Treatment of 2,3-dibromo-1,1-diphenyl-2-propen-1-ol in alcoholic solution with 2,4-dinitrophenylhydrazine in presence of sulfuric acid gave the 2,5-dinitrophenylhydrazone of 2-bromo-3,3-diphenylacrolein, m.p. 245-246° (from acetic acid).

Found %: N 11.90; 11.76
$C_{21}H_{15}BrN_4O_4$. Calculated %: N 11.98

When concentrated hydrochloric acid was added to a hot solution of 2,3-dibromo-1,1-diphenyl-2-propen-1-ol in acetic acid, after a few minutes there was a crystalline precipitate of 1,2-dibromo-3-chloro-3,3-diphenylpropene, m.p. 137-138° (from acetic acid).

Found %: C 46.15; 46.19; H 2.87; 2.97
$C_{15}H_{11}Br_2Cl$. Calculated %: C 46.50; H 2.86

In a similar way, reaction with hydrobromic acid gave 1,2,3-tribromo-3,3-diphenylpropene, m.p. 152-153° (from acetic acid).

Found %: C 41.98; 42.90; H 2.53; 2.48
$C_{15}H_{11}Br_3$. Calculated %: C 41.78; H 2.55

1,2-Dibromo-3-phenylindene. A few drops of 70% perchloric acid were added to a warm solution of 5 g of 2,3-dibromo-1,1-diphenyl-2-propen-1-ol in 20 ml of acetic acid, and the mixture was heated for a few minutes at 105-110°. When the mixture cooled, a crystalline precipitate (3.2 g) of 1,2-dibromo-3-phenylindene formed; m.p. 82-83° (from alcohol).

Found %: C 51.17; 51.19; H 3.00; 3.06; Br 45.72
$C_{15}H_{10}Br_2$. Calculated %: C 51.42; H 2.86; Br 45.71

When a solution of 1,2,3-tribromo-3,3-diphenylpropene in 90% acetic acid was boiled for several hours, 1,2-dibromo-3-phenylindene was again obtained; m.p. 82-83° (from alcohol). The product showed no melting point depression in admixture with the 1,2-dibromo-3-phenylindene obtained in the preceding experiment.

Oxidation of 2.2 g of 1,2-dibromo-3-phenylindene with potassium permanganate (3.2 g) in presence of magnesium oxide in aqueous-acetone solution at room temperature gave 0.8 g of o-benzoylbenzoic acid, m.p. 127-128° (from benzene). The product showed no melting point depression in admixture with o-benzoylbenzoic acid prepared from phthalic anhydride and benzene.

2,3,3-Trichloro-1-phenyl-2-propen-1-ol. A mixture of 15 g of 2,3,3-trichloroacrylophenone, 15 g of aluminum isopropoxide, and 50 ml of isopropyl alcohol was heated for five hours, acetone being distilled off. The reaction mixture was decomposed cautiously with dilute sulfuric acid, and was extracted with chloroform. Vacuum distillation gave 13.2 g of 2,3,3-trichloro-1-phenyl-2-propen-1-ol, b.p. 119-113° (1.5 mm); n_D^{20} 1.5820; d_4^{20} 1.4225; Found MR 55.72; Calculated MR 56.72.

Found %: C 45.72; 45.69; H 2.99; 3.09

$C_9H_7Cl_3O$. Calculated %: C 45.47; H 2.94

α-Chlorocinnamic Acid. Heating of an acetic acid solution of 5 g of 2,3,3-trichloro-1-phenyl-2-propen-1-ol in presence of hydrochloric acid for four hours gave 0.1 g of α-chlorocinnamic acid, m.p. 139-140° (from petroleum ether). When the mixture was heated for 25 hours, the yield of α-chlorocinnamic acid was 75%.

SUMMARY

1. A study was made of the possibility of allyl anionotropic rearrangement in the systems $RR'C(OH)CH{=}CX_2$, $RR'C(OH)CX{=}CHX$ and $RR'C(OH)CX{=}CX_2$, X being halogen. It was shown that when the substituents are alkyl groups rearrangement does not occur.

2. It was shown that rearrangement occurs in these systems when R = Ar and R' = H.

3. It was found that $CCl_2{=}CH{-}CH(OC_2H_5)CN$ does not undergo allyl anionotropic rearrangement, but readily undergoes allyl prototropic rearrangement in presence of triethylamine.

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* T. p. = C. B. Translation pagination.

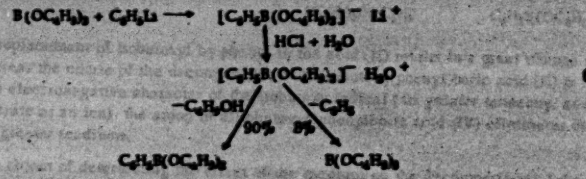
ORGANOBORON COMPOUNDS

COMMUNICATION 5. PREPARATION OF ISOBUTYL ESTERS OF BENZENEBORONIC AND DIPHENYLBORINIC ACIDS WITH THE AID OF PHENYLLITHIUM

B. M. Mikhailov and P. M. Aronovich

In a previous paper [1] we have described the reactions of phenyllithium with isobutyl esters of boric acid and benzeneboronic acids, which result in the formation of complex salts: lithium triisobutoxy(phenyl)borate and lithium diisobutoxydiphenylborate*. Further study of these reactions has shown that they can be applied to the preparation of benzeneboronic acid (or its esters) and esters of diphenylborinic acid.

It was found that, as might be expected, lithium triisobutoxy(phenyl)borate (I) is converted by treatment with mineral acids into benzeneboronic acid, but, in addition, a small amount (8%) of boric acid is formed. It is clear that the triisobutoxy(phenyl)boric acid (II) formed from the lithium salt (I) is decomposed with elimination of an alcohol or benzene with formation of esters of benzeneboronic or boric acid, respectively, this being then hydrolyzed to the corresponding acid:



When the products of the reaction between phenyllithium and triisobutyl borate are treated directly with hydrochloric acid, benzeneboronic acid can be obtained in 82% yield without isolating the salt (I). Also, if the reaction mixture is treated with dry hydrogen chloride, a good yield of diisobutyl benzeneboronate can be obtained.

The fact that the synthesis of an areneboronic ester from a trialkyl borate and an aryllithium passes through the stage of a salt of a complex boric acid suggests that the reaction between a trialkyl borate and an organomagnesium compound may occur by a similar mechanism and not as a metathetic reaction, as it has usually been regarded:

$$B(OAlk)_3 + RMgX \longrightarrow RB(OAlk)_2 + AlkOMgX.$$

The synthesis of boronic esters with the aid of Grignard reagents may then be expressed as follows:

$$B(OAlk)_3 + RMgX \longrightarrow [RB(OAlk)_3]^-MgX^+ \longrightarrow [RB(OAlk)_3]^-H_3O^+ \longrightarrow RB(OAlk)_2$$

* As there is no recognized system of nomenclature for compounds of this type, they are named here by an adaptation of the nomenclature for inorganic complex compounds. — Publisher.

Lithium diisobutoxydiphenylborate (III) differs greatly in properties from the complex borate (I). The complex salt (III) required for this investigation was prepared by the addition of lithium isobutoxide to isobutyl diphenylborinate, which was obtained by the action of phenylmagnesium bromide on triisobutyl borate [2]

$$[(C_6H_5)_2BOC_4H_9 + C_4H_9OLi \rightarrow [(C_6H_5)_2B(OC_4H_9)_2]^- Li^+ \qquad (III)$$

This method gives the complex borate (III) in the pure state and in high yield.

When an aqueous solution of lithium diisobutoxydiphenylborate (III) was treated with dilute hydrochloric acid, a mixture of isobutyl diphenylborinate and benzeneboronic acid was obtained, with a considerable preponderance of the second (28% and 62% yield respectively). The same results were obtained by decomposition of the products of reaction between phenyllithium and diisobutyl benzeneboronate with hydrochloric acid without isolation of the intermediate complex compound (III) in the pure state. Thus, the diisobutoxydiphenylboric acid (IV) formed by acidification of a solution of the salt (III) decomposes like the acid (II) with elimination of an alcohol or benzene, but in this case the second course of decomposition is predominant:

$$[(C_6H_5)_2B(OC_4H_9)_2]^- Li^+ \xrightarrow{HCl + H_2O} [(C_6H_5)_2B(OC_4H_9)_2]^- H_3O^+ \qquad (IV)$$

$$-C_4H_9OH \qquad -C_6H_6$$

$$28\% \qquad 62\%$$

$$(C_6H_5)_2BOC_4H_9 \qquad C_6H_5B(OC_4H_9)_2$$

Hence, replacement of isobutoxyl by phenyl in the acid (II) results in a great change in the properties of the acid. Whereas the course of the decomposition of triisobutoxy(phenyl)boric acid (II) is in full accord with the relatively high electronegative character of the isobutoxy radical (its greater tendency, as compared with that of phenyl, to separate as an ion) the anion of diisobutoxydiphenylboric acid (IV) eliminates the less electronegative phenyl as an ion with greater readiness.

With the object of determining the effect of the medium on the decomposition of the diisobutoxydiphenylborate anion, experiments were carried out on the effect of dry hydrogen chloride on the complex salt (III). It was found that, under these conditions, the salt (III) is converted mainly into the diphenylborinic ester (82% yield), the benzeneboronic ester being obtained in only 5% yield.

$$[(C_6H_5)_2B(OC_4H_9)_2]^- Li^+ \xrightarrow{HCl} [(C_6H_5)_2B(OC_4H_9)_2]^- H^+ \qquad (V)$$

$$-C_4H_9OH \qquad -C_6H_6$$

$$82\% \qquad 5\%$$

$$(C_6H_5)_2BOC_4H_9 \qquad C_6H_5B(OC_4H_9)_2$$

Hence, replacement of the ononium ion of diisobutoxydiphenylboric acid (IV) by a proton — the acid (V) — has a marked effect on the character of its decomposition.

This method — the decomposition of the complex borate (III) with dry hydrogen chloride — is of preparative importance. When the products of reaction between phenyllithium and a benzeneboronic ester are decomposed in this way, the pure diphenylborinic ester can be obtained in 70% yield without isolation of the salt (III).

EXPERIMENTAL

Action of Hydrochloric Acid on Lithium Triisobutoxy(phenyl)borate

To a solution of 6.28 g (0.02 mole) of lithium triisobutoxy(phenyl)borate (prepared by the addition of lithium isobutoxide to diisobutyl benzeneboronate [1]) in 10 ml of water, 3 ml of 30% hydrochloric acid was added, and the mixture was treated four times with ether. Ether was distilled from the extract, 15 ml of water was added to the residual solution, and isobutyl alcohol was distilled off together with the water. The residue was cooled, and the

precipitate of benzeneboronic acid was filtered off and dried (1.97 g); a further 0.22 g of benzeneboronic acid was extracted from the filtrate with ether. The total yield of benzeneboronic acid was 90%; the unpurified acid melted at 207-210°.

Caustic soda was added to the aqueous solution until it became weakly alkaline, and it was then evaporated down to about 10 ml. Methanol (20 ml) was added, the mixture was neutralized exactly with acid, and 2 g of mercuric chloride was added. The mixture remained neutral, so that benzeneboronic acid was absent. After addition of excess of mannitol, the boric acid present was titrated with caustic soda, the amount found being 0.097 g, i.e. 7.8%.

Benzeneboronic Acid and its Isobutyl Ester

A solution of phenyllithium prepared from 17.3 g (0.11 mole) of bromobenzene, 1.6 g of lithium, and 175 ml of ether was cooled to −5° and was then gradually cooled still further and stirred mechanically while addition was made of a solution of 23 g (0.1 mole) of triisobutyl borate in 50 ml of ether. The greater part of the solution was added at below −50°, the duration of the addition being 20-40 minutes. The reaction mixture was stirred for five hours at −70°, and was then left in a cooling bath. On the next day the mixture was acidified with 20% hydrochloric acid, the ether layer was separated, the aqueous layer was treated twice with ether, and solvent was distilled from the combined ethereal solutions. Water (50 ml) was added to the residue, and isobutyl alcohol was distilled off together with the water. The residue was cooled, and benzeneboronic acid was filtered off and dried. The yield was 10 g, i.e. 82%; the unpurified acid melted at 208-215°.

For the preparation of diisobutyl benzeneboronate, the reaction was carried out as described above, but the reaction mixture was saturated with dry hydrogen chloride, ether was distilled off, and the precipitate present was filtered off and washed with benzene. Isobutyl alcohol and benzene were distilled from the filtrate, and the residue was fractionally distilled, the product being 16 g (68%) of ester, b. p. 116-117° (5 mm) and d_4^{20} 0.9243.

Found %: C_6H_5 32.78; B 4.52

$C_6H_5B(OC_4H_9)_2$. Calculated %: C_6H_5 32.93; B 4.62

Lithium Diisobutoxydiphenylborate

In a nitrogen atmosphere, 11.5 ml (0.125 mole) of absolute isobutyl alcohol was added to 77 ml (0.1 mole) of a cooled (ice water) mechanically stirred 1.3 N benzene solution of butyllithium. To the resulting clear solution of lithium isobutoxide, which was again cooled with ice water, 26.2 g (0.11 mole) of isobutyl diphenylborinate diluted with 50 ml of ether was added over a period of 30 minutes. The resulting solution was stirred for three hours at 0°, and the solvent was distilled off under reduced pressure in a current of nitrogen. When the mass became thick, the capillary was raised and the nitrogen was passed above the mixture, the flask being heated in a boiling water bath. After the removal of solvents was complete, the residue was mixed with 50 ml of hexane and filtered. The residue was washed on the filter with 40 ml of hexane and vacuum-dried. The yield of lithium diisobutoxydiphenyl borate was 24.8 g (78%).

Found %: Li 2.24; C_6H_5 48.27; B 3.32

$(C_6H_5)_2B(OC_4H_9)_2Li$. Calculated %: Li 2.19; C_6H_5 48.46; B 3.40

Action of Hydrochloric Acid on Lithium Diisobutoxydiphenylborate

Hydrochloric acid (20%) was added to a cooled (ice water) stirred solution of 15.9 g (0.05 mole) of lithium diisobutoxydiphenylborate in 50 ml of ether until it reacted acid. The ether layer was separated, the aqueous layer was treated twice with ether, and ether and isobutyl alcohol were distilled from the ether extracts. The residue was mixed with 20 ml of isopentane and filtered; the residue of benzeneboronic acid was washed with isopentane and dried (yield 3.2 g). Isopentane was distilled from the filtrate, and vacuum distillation of the residue gave 3.3 g (27.8%) of isobutyl diphenylborinate, b. p. 142-145° (6 mm). A residue of 0.6 g of benzeneboronic acid remained in the flask; the total yield of benzeneboronic acid was 62.3%.

Action of Hydrogen Chloride on Lithium Diisobutoxydiphenylborate

Dry hydrogen chloride was passed through a solution of 15.9 g (0.05 mole) of lithium diisobutoxydiphenylborate in 50 ml of ether for one hour. Ether was distilled off, and the precipitate of lithium chloride was filtered off and washed with benzene. Distillation of the filtrate gave 10.3 g of a fraction boiling at 158-164° (8 mm).

Found %: C_6H_5 63.0; B 4.51.

Calculation showed that the mixture contained 0.87 g of $C_6H_5B(OC_4H_9)_2$ and 9.73 g of $(C_6H_5)_2BOC_4H_9$. The yield of diisobutyl benzeneboronate was thus 4.9%, and that of isobutyl diphenylborinate 81.7%.

Action of Phenyllithium on Diisobutyl Benzeneboronate

a) Decomposition with Hydrochloric Acid. Under the condition described above for the preparation of benzeneboronic acid, 23.4 g (0.1 mole) of diisobutyl benzeneboronate was added to an ethereal solution of phenyllithium prepared from 17.3 g (0.11 mole) of bromobenzene, 1.6 g of lithium, and 175 ml of ether. The resulting clear solution was acidified with 20% hydrochloric acid. Ether and isobutyl alcohol were distilled off, and the residue was vacuum-fractionated through a column, yielding Fraction I [0.9 g, b.p. 112-116° (6 mm).] which was a mixture of diphenyl with a little diisobutyl benzeneboronate, Fraction II [2.9 g, b.p. 117-119° (6 mm)], which was diisobutyl benzeneboronate, and Fraction III [b.p. 143-144° (6 mm).] which was isobutyl diphenylborinate, obtained in 26.1% yield (6.2 g). The residue in the flask (5.8 g) was benzeneboronic acid. The overall yield of benzeneboronic acid and its ester was 60.2%.

b) Decomposition with Hydrogen Chloride. Reaction between equimolecular amounts of diisobutyl benzeneboronate and phenyllithium was carried out as described above. The reaction mixture was saturated with hydrogen chloride, ether was distilled off, and lithium chloride was filtered off and washed with benzene. Benzene and isobutyl alcohol were distilled from the filtrate, and vacuum fractionation of the residue gave 1.91 g of Fraction I, boiling up to 152° (8 mm), and 16.97 g of Fraction II, b.p. 153-158° (8 mm).

Fraction I. Found %: C_6H_5 38.60; B 2.93
Fraction II. Found %: C_6H_5 62.50; B 4.53

$C_6H_5B(OC_4H_9)_2$. Calculated %: C_6H_5 32.93; B 4.62
$(C_6H_5)_2BOC_4H_9$. Calculated %: C_6H_5 64.75; B 4.54

Calculation shows that Fraction I contained 0.1 g of diisobutyl benzeneboronate and 1.1 g of isobutyl diphenylborinate, the remainder being biphenyl. Fraction II contained 1.2 g of $C_6H_5B(OC_4H_9)_2$ and 15.73 g of $(C_6H_5)_2BOC_4H_9$.

Hence, the yield of diisobutyl benzeneboronate was 1.3 g (5.5%), and the yield of isobutyl diphenylborinate was 16.9 g (71%). The analyses were carried out by the method of Wittig and coworkers [3]. All operations with phenyllithium were carried out in an atmosphere of dry nitrogen, and the complex compounds were isolated with exclusion of moisture.

SUMMARY

1. When lithium triisobutoxy(phenyl)borate was treated with hydrochloric acid, benzeneboronic acid and a little boric acid were formed.

2. When lithium diisobutoxydiphenylborate was treated with hydrochloric acid, the main product was benzeneboronic acid, isobutyl diphenylborinate being formed, but in smaller amount. In the decomposition of lithium diisobutoxydiphenylborate with hydrogen chloride, isobutyl diphenylborinate was formed almost exclusively.

3. In the reaction of triisobutyl borate with phenyllithium, the yield of benzeneboronic acid was 82%.

4. Reaction of diisobutyl benzeneboronate with phenyllithium, followed by decomposition of the reaction products with hydrogen chloride, resulted in the formation of isobutyl diphenylborinate in 70% yield.

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ACYLATION OF AMINOALKYL-PHOSPHONIC AND -PHOSPHONOTHIONIC ACIDS WITH CHLOROFORMIC ESTERS

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Investigators have recently shown great interest in carbamic acid derivatives because of their physiological activity, which is often very specific. It appeared to us that it would be of interest to synthesize carbamic esters having various phosphorus-containing groups substituted in an N-alkyl radical. Compounds of this kind can be readily prepared from aminoalkylphosphonic acids [1] or their esters by acylation with chloroformic esters.

We have previously studied [2] the acylation of aminoalkylphosphonic acids and esters with the acid chlorides and anhydrides of carboxylic acids. They were found to be somewhat more difficult to acylate than the usual amino carboxylic acids, but reaction nevertheless proceeded fairly readily. We have found that chloroformic esters also react readily with aminoalkyl-phosphonic and -phosphonothionic esters. When the reaction is carried out in a benzene medium in presence of excess of pyridine, the phosphorus grouping is not affected and the corresponding carbamic acid derivatives are formed:

A few minutes after the addition of the chloroformic ester to the mixture of aminoalkyl-phosphonic or -phosphonothionic ester, pyridine, and benzene, pyridine hydrochloride begins to separate and gradually forms into crystals. If necessary in order to bring the reaction to completion, the mixture is heated at 60-70° for 20-30 minutes. After removal of excess of pyridine and pyridine hydrochloride by washing with water, drying of the benzene solution, removal of solvent by distillation, and vacuum distillation of the residue, (alkoxycarbonyl-amino)alkyl-phosphonic and -phosphonothionic esters are obtained, usually in 40-80% yield. The constants of the substances obtained are given in the table.

We showed, on the basis of one example, that free aminoalkylphosphonic acids can also be acylated with chloroformic esters, but the reaction must then be carried out under Schotten-Baumann conditions.

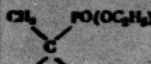
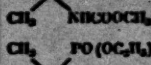
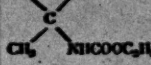
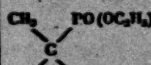
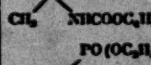
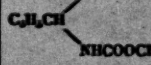
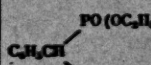
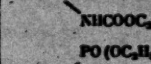
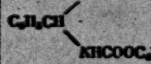
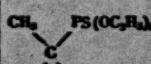
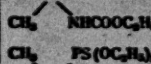
All of the urethans obtained are readily soluble in alcohol, ether, and other organic solvents, but, with the exception of No. 1 and 2, they are insoluble in water.

We have already described [1] the original aminoalkyl-phosphonic and -phosphonothionic esters. In the present investigation we have prepared also O,O-diethyl α-aminobenzylphosphonothionate, which was described previously only in the form of the picrate. The ester is readily isolated by treating the picrate with alkali and extracting the alkaline solution with ether. Its constants are given in the table (No. 11).

EXPERIMENTAL

1. Diethyl 1-(Methoxycarbonylamino)-1-methylethylphosphonate. Methyl chloroformate (1.2 g) was added dropwise to a mixture of 1.95 g of diethyl 1-amino-1-methylethylphosphonate, 15 ml of pyridine, and 20 ml of benzene. The reaction was carried out at 2-3°. As the chloroformic ester was added, crystals of pyridine hydrochloride began to be precipitated on the walls of the flask. When the separation of crystals stopped, they were removed from the solution. An equal volume of water was added to the solution, and the mixture was shaken vigorously. The benzene layer was separated, and the aqueous layer was again extracted with 10 ml of fresh benzene. The combined benzene layers were washed with a 5% solution of sodium carbonate and dried with sodium sulfate. Benzene was then distilled off, and the residue was vacuum-distilled.

TABLE

No.	Formula	B.p. in °C (p in mm)	M.p. (°C)	n_D^{20}	d_4^{20}	MR Found	MR Calculated
1		104 (2)	—	1.4505	1.1507	50.2	50.9
2		127—128 (3)	—	1.4497	1.1154	61.1	61.5
3		137—138 (3)	58—59	—	—	—	—
4		— —	104—106	—	—	—	—
5		— —	68—69	—	—	—	—
6		179 (3)	45—46	—	—	—	—
7		107—108 (3)	—	1.4788	1.1147	72.0	71.9
8		120—121 (3)	—	1.4747	1.0702	81.2	81.2
9		180 (3)	49—50	—	—	—	—
10		158—160 (2)	—	1.5197	1.1308	96.6	96.1
11		129—130 (3)	—	1.5473	1.1478	71.8	71.2

The product, amounting to 0.54 g (21.3%), was a clear yellowish sirupy liquid, b.p. 104° (2 mm); n_D^{20} 1.4508; d_4^{20} 1.1507; Found MR 59.2; Calculated MR 59.9. It was soluble in water, alcohol, ether, and other organic solvents.

Found %: N 5.2; 5.4; P 12.1; 12.0
$C_7H_{18}NPO_3$. Calculated %: N 5.5; P 12.2

2. Diethyl 1-(Ethoxycarbonylamino)-1-methylethylphosphonate. This was prepared from a mixture of 5.85 g of diethyl 1-amino-1-methylethylphosphonate, 15 ml of pyridine, 30 ml of benzene, and 5.1 g of ethyl chloroformate. The reaction temperature was 5-8°. The procedure was as in the preceding experiment. The product, amounting to 5.65 g (70.5%), had b.p. 127-128° (3 mm); n_D^{20} 1.4497; d_4^{20} 1.1154; Found MR 64.4; Calculated MR 64.5. It was soluble in water, alcohol, ether, and other organic solvents.

Found %: C 45.1; 45.2; H 8.3; 8.5; N 5.2; 5.2; P 11.4; 11.4
$C_8H_{18}NPO_4$. Calculated %: C 44.9; H 8.3; N 5.2; P 11.6

3. Diethyl 1-(Isobutoxycarbonylamino)-1-methylethylphosphonate. This was prepared from a mixture of 1.95 g of diethyl 1-amino-1-methylethylphosphonate, 15 ml of pyridine, 30 ml of benzene, and 1.75 g of isobutyl chloroformate, which was heated for 30 minutes at a bath temperature of 50-60°. The further treatment of the reaction mixture was the same as in the preceding experiments. The product, amounting to 1.9 g (64%), boiled at 137-138° (3 mm). After being distilled, the substance solidified to crystals, m. p. 58-59°. This substance is insoluble in water, but readily soluble in alcohol, ether, and other organic solvents.

Found %: C 49.0; 49.2; H 8.7; 8.7; N 4.8; 4.8; P 10.3; 10.4
$C_{11}H_{24}NPO_4$. Calculated %: C 48.8; H 8.8; N 4.7; P 10.5

4. Diethyl α-(Methoxycarbonylamino)benzylphosphonate. This was prepared from 0.85 g of diethyl α-aminobenzylphosphonate, 5 ml of pyridine, 10 ml of benzene, and 0.4 g of methyl chloroformate. The product, amounting to 0.4 g (38%), was a colorless substance. It was recrystallized from ether; m.p. 104-106°. It did not dissolve in water, but was readily soluble in organic solvents.

Found %: C 52.2; 52.2; H 6.8; 7.0; P 10.5; 10.2
$C_{11}H_{16}NPO_5$. Calculated %: C 51.8; H 6.7; P 10.3

5. Diethyl α-(Ethoxycarbonylamino)benzylphosphonate. This was prepared from a mixture of 1.2 g of diethyl α-aminobenzylphosphonate, 7.5 ml of pyridine, 15 ml of benzene, and 0.75 g of ethyl chloroformate. The procedure was the same as in the preceding experiments. The residue remaining after removal of benzene was crystallized from ether, the product being 0.95 g (61%) of a colorless crystalline substance, m. p. 68-69°. This substance is not soluble in water, but readily dissolves in alcohol, ether, and other organic solvents.

Found %: C 53.5; 53.5; H 7.1; 7.3; N 4.3; 4.3; P 9.4; 9.4
$C_{12}H_{18}NPO_5$. Calculated %: C 53.3; H 7.0; N 4.4; P 9.8

6. Diethyl α-(Isobutoxycarbonylamino)benzylphosphonate. This was prepared from a mixture of 1.2 g of diethyl α-aminobenzylphosphonate, 7.5 ml of pyridine, 15 ml of benzene, and 0.87 g of isobutyl chloroformate, the procedure being the same as in the preceding experiments. The product, amounting to 0.85 g (50%), was a colorless sirupy liquid, b.p. 179° (3 mm). After being distilled, the substance solidified to crystals melting at 45-46°. This substance is insoluble in water, but readily soluble in alcohol, ether, and other organic solvents.

Found %: C 56.1; 55.9; H 7.6; 7.6; N 3.9; 4.0; P 8.7; 8.9
$C_{15}H_{24}NPO_5$. Calculated %: C 56.0; H 7.6; N 4.1; P 9.0

7. 0,0-Diethyl 1-(Ethoxycarbonylamino)-1-methylethylphosphonothioate. Ethyl chloroformate (1.5 g) was added dropwise to a mixture of 2.1 g of 0,0-diethyl 1-amino-1-methylphosphonothioate, 15 ml of pyridine, and 30 ml of benzene. The temperature of the reaction mixture then rose from 18° to 27°, and pyridine hydrochloride was gradually precipitated on the walls of the flask. The mixture was then heated in a bath for 30 minutes at 50-60°. When cool, the liquid was separated from the crystals and washed with an equal amount of water. The aqueous solution was extracted with a fresh portion of benzene. The combined benzene solutions were washed with 5% sodium carbonate solution and with water, and were then dried over sodium sulfate. The residue remaining after removal of benzene was vacuum-distilled and gave 1.6 g (57%) of a clear colorless liquid, b.p. 107-108° (3 mm); n_D^{18} 1.4788; d_4^{20} 1.1147; Found MR 72.0; Calculated MR 72.0. It did not dissolve in water, but was readily soluble in organic solvents.

Found %: C 42.1; 42.0; H 7.6; 7.8; N 4.7; 4.6; P 11.0; 11.3; S 11.0; 11.5

$C_{12}H_{28}NPSO_3$. Calculated %: C 42.4; H 7.8; N 4.9; P 10.9; S 11.3

8. 0,0-Diethyl 1-(Isobutoxycarbonylamino)-1-methylethylphosphonothioate. This was prepared from a mixture of 2.1 g of 0,0-diethyl 1-amino-1-methylethylphosphonothioate, 15 ml of pyridine, 30 ml of benzene, and 1.75 g of isobutyl chloroformate, the procedure being as in the preceding experiment. The product, amounting to 1.71 g (53%), was a clear colorless liquid, b.p. 120-123° (3 mm); n_D^{20} 1.4747; d_4^{20} 1.0792; Found MR 81.2; Calculated MR 81.2.

Found %: C 46.4; 46.2; H 8.2; 8.2; N 4.3; 4.3; P 9.3; 9.8; S 10.3; 10.4

$C_{12}H_{28}NPSO_3$. Calculated %: C 46.3; H 8.4; N 4.5; P 9.9; S 10.3

9. 0,0-Diethyl α-(Ethoxycarbonylamino)benzylphosphonothioate. This was prepared from a mixture of 1.3 g of 0,0-diethyl α-aminobenzylphosphonothioate, 7.5 ml of pyridine, 15 ml of benzene, and 0.75 g of ethyl chloroformate, the procedure being as in the preceding experiments. The product, amounting to 1 g (60%), boiled at 160° (3 mm) and melted at 49-50°. It was found to be insoluble in water, but readily soluble in alcohol, ether, and other organic solvents.

Found %: C 51.2; 51.0; H 6.8; 6.8; N 3.9; 3.7; P 9.2; 9.2; S 10.1; 10.2

$C_{14}H_{22}NPSO_4$. Calculated %: C 50.7; H 6.7; N 4.2; P 9.4; S 9.7

10. 0,0-Diethyl α-(Isobutoxycarbonylamino)benzylphosphonothioate. This was prepared from a mixture of 0.54 g of 0,0-diethyl α-aminobenzylphosphonothioate, 3 ml of pyridine, 6 ml of benzene, and 0.36 g of isobutyl chloroformate, the procedure being as in the preceding experiments. The product, amounting to 0.22 g (30.5%), was a colorless sirupy liquid, b.p. 158-160° (2 mm), n_D^{20} 1.5197; d_4^{20} 1.1308; Found MR 96.6; Calculated MR 98.1.

Found %: C 53.0; 52.9; H 7.2; 7.2; P 8.4; 8.2; S 9.3; 9.2

$C_{16}H_{26}NPSO_4$. Calculated %: C 53.4; H 7.3; P 8.6; S 8.9

11. 0,0-Diethyl α-Aminobenzylphosphonothioate. A solution of 0.25 g of caustic soda in a mixture of 10 ml of ethanol and 10 ml of ether was added to 3 g of the picrate of 0,0-diethyl α-aminobenzylphosphonothioate [1], m.p. 176-178°. The mixture was heated in a bath for five minutes at 60-70°. When the mixture was cool, 3 ml of water was added (until the precipitate dissolved), and then 5 ml of ether. The mixture was agitated vigorously, the ether layer was separated, and the aqueous layer was again extracted with ether several times. The ether solution was washed with small portions of water until picric acid had been removed completely. It was then dried over sodium sulfate. After removal of ether, the residue was vacuum-distilled. The product, amounting to 1.1 g (68%), was a clear yellowish liquid, b.p. 129-130° (3 mm); n_D^{20} 1.5473; d_4^{20} 1.1478; Found MR 71.6; Calculated MR 71.2.

Found %: C 51.0; 51.0; H 6.9; 6.9; N 5.3; 5.2; P 12.1; 11.8; S 12.5; 12.8

$C_{11}H_{18}NPSO_3$. Calculated %: C 50.9; H 7.0; N 5.4; P 11.9; S 12.4

SUMMARY

The introduction of N-alkoxycarbonyl into aminoalkyl-phosphonic and -phosphonothionic esters was investigated. It was found that reaction between aminoalkyl-phosphonic and -phosphonothionic esters and chloroformic esters in presence of pyridine resulted in the formation of the corresponding urethans.

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[2] M. I. Kabachnik and T. Ya. Medved, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1126, (1953) (T.p. 969)*. T. Ya. Medved and M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1013 (1954); (T.p. 907)*.

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* T. p. = C. B. Translation pagination.

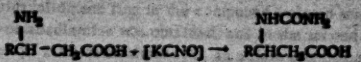
PREPARATION AND REACTIONS OF SOME DERIVATIVES OF 3-UREIDONONANOIC ACID

V. M. Rodionov* and V. K. Zverykina

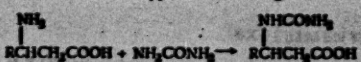
When amides of β-acylamino acids are treated with alkaline hypobromite, various complex and interesting reactions occur, which have been studied in our laboratory for various β-acylamino acid amides containing an aliphatic [1-3] or aromatic [4, 5] radical, and also for various acylureas. These investigations showed that it is possible to pass from β-amino acids to derivatives of imidazolidinone, hydantoin, oxadiazolinone, α-amino acids, and carboxylic acids. It was of interest to extend our study of the reaction to amides of β-ureido acids, in which, as a result of the action of hypobromite both on the amide and the ureide groups, the formation of heterocyclic compounds of the triazine and triazole series could be expected. With this object, we synthesized some amides of β-ureido, β-(3-alkylureido), and β-(3-arylureido) acids, which, for practical purposes, have not been described previously in the literature**.

Three methods are known for the preparation of ureido acids, and the yields obtained by the use of these usually range from 75% to 90%.

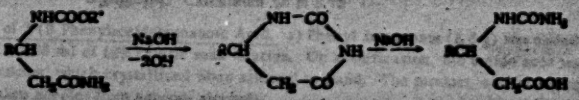
1) The general and very simple method due to Lendfeld and Stiegliz [8] (action of KCNO and RNCO on β-amino acids):



2) The long-known method due to Lippich [6] (heating the β-amino acid with a large excess of urea):



3) Our new method [9] for the preparation of β-ureido acids from amides of β-alkoxycarbonylamino acids by heating them with 5-10% caustic soda solutions:



The last method, which is somewhat more complicated than the others, has been used mainly for the characterization of β-amino acids, and also for the identification of synthesized compounds and the determination of their structures. It was of interest to extend this reaction to alkylated and arylated amides of β-alkoxycarbonylamino acids, and so make it possible to prepare β-(3-alkylureido) and β-(3-arylureido) acids without the use of alkyl and aryl isocyanates, which are not always readily accessible. Our experiments with the anilide and methylamide of 3-(ethoxycarbonylamino)nonanoic acid showed that the reaction is general and enabled us to extend its field of application. 3-(3-Alkylureido)- and 3-(3-arylureido)-nonanoic acids were prepared in 75-80% yield.

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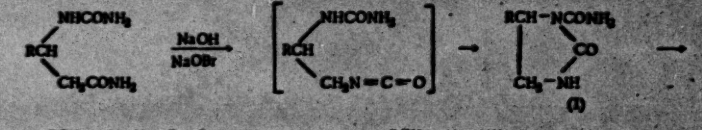
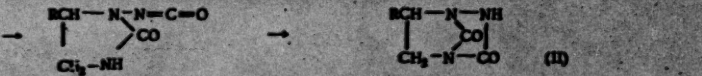
* Deceased.

** In 1952, in the preparation of 3-(2-naphthyl)-3-ureidopropionic acid by Lippich's method [6], Kurtev [7] noted the formation of about 4% of the amide of this acid.

For the preparation of amides of β-ureido acids we decided to use the synthesis via the acid chloride, which we have generally applied in the preparation of amides of acylated β-amino acids [10]. By this method we prepared amides of 3-ureido- and 3-(3-phenylureido) nonanoic acids in 70% yield. It is true that this reaction was accompanied by partial cyclization of the amide with elimination of ammonia and formation of a hydrouracil, but the compounds formed differed in properties and their separation presented no difficulty. 3-Ureidononanamide has a feebly alkaline reaction and is readily dissolved by 12% hydrochloric acid, from which it can be recovered unchanged by addition of caustic soda, whereas 6-hexylhydrouracil is a feebly acid substance, sparingly soluble in water and readily precipitated when its alkaline solution is acidified. A single recrystallization is sufficient to purify the substances obtained. For the separation of 3-(3-phenylureido)nonanamide and 6-hexyl-3-phenylhydrouracil, use was made of their differing solubility in alcohol.

In the Hofmann reaction with 3-ureidononanamide, a neutral substance melting at 121° was isolated for which elementary analysis and molecular weight determination suggested that its formula could be (I) or (II), on the assumption that the process occurs according to the following scheme:





Determination of active hydrogen by Terentyev's method confirmed the correctness of formula (I). The presence of an imidazolidinone ring in the compound isolated was established by acid and alkaline hydrolysis: in the first case 1,2-octanediamine was obtained, and in the second 4-hexyl-2-imidazolidinone. Apart from 1-carbamoyl-5-hexyl-2-imidazolidinone (I), an acidic amorphous substance containing nitrogen was also isolated. This substance was obtained in various experiments, and it had a rather wide, but always the same, decomposition temperature range, 127-160°. It corresponded in elementary composition to the formula $C_9H_{16}O_3N_2$.

EXPERIMENTAL

Preparation of 3-(Ethoxycarbonylamino)nonananilide. The ethoxycarbonyl derivative (2 g) was treated at 0° with 1.4 g of thionyl chloride, and the product was cooled while an ethereal solution of aniline was added. The anilide, amounting to 2.35 g (89%), melted at 152° (fine colorless needles from alcohol).

Found %: N 8.70; 8.66

$C_{20}H_{32}O_3N_2$. Calculated %: N 8.75

Preparation of 3-(3-Phenylureido)nonanoic Acid. a) Phenyl isocyanate (5.6 g) was added dropwise to 10 g of the amino acid in 100 ml of 12% caustic soda solution. On acidification, the ureido acid was precipitated in the form of an emulsion, which crystallized when allowed to stand. The product, amounting to 8.5 g (74%), melted at 106° (long colorless needles from aqueous alcohol).

Found %: N 9.57; 9.72

$C_{16}H_{24}O_3N_2$. Calculated %: N 9.59

b) 3-(Ethoxycarbonylamino)nonananilide (0.5 g) was boiled for seven hours with a 7.5% solution of caustic soda in 50% alcohol. The product was 0.34 g (80%) of 3-(3-phenylureido)nonanoic acid, m.p. 105°. In admixture with the product of Experiment a it melted at 105°.

Preparation of 3-(Ethoxycarbonylamino)-N-methylnonanamide. The methylamide was prepared under the same conditions as the anilide. From 1 g of the ethoxycarbonyl derivative, 0.72 g (69%) of the methylamide, m.p. 125°, was obtained (colorless flat needles from alcohol).

Found %: C 60.39; 60.70; H 10.21; 10.40; N 10.27

$C_{13}H_{26}O_3N_2$. Calculated %: C 60.48; H 10.08; N 10.85

Preparation of 3-(3-Methylureido)nonanoic Acid. The methylamide (0.1 g) was boiled for two hours with a 7% solution of caustic soda. Acidification of the cooled solution gave an emulsion, which crystallized by the next day. The product was 0.28 g (80.4%) of 3-(3-methylureido)nonanoic acid, m.p. 103-104° (long thin needles from water).

Found %: C 57.32; 57.75; H 9.67; 9.66; N 12.30; 12.28
$C_{11}H_{22}O_3N_2$. Calculated %: C 57.39; H 9.56; N 12.17

Preparation of 6-Hexyl-3-phenylhydrouracil. 3-(3-Phenylureido)nonanoic acid (1 g) was boiled for two hours with 20 ml of 17% hydrochloric acid. Evaporation of the solution gave 0.71 g (75%) of 6-hexyl-3-phenylhydrouracil, m.p. 210° (long needles from alcohol).

Found %: C 69.84; 70.04; H 8.32; 8.20; N 10.69
$C_{16}H_{22}O_2N_2$. Calculated %: C 70.09; H 8.03; N 10.22

Preparation of 3-(3-Phenylureido)nonanamide. A mixture of 4.6 g of the ureido acid and 5 ml of thionyl chloride was heated for three hours at 40°. The hydrochloride of the acid chloride was washed free from excess of thionyl chloride with absolute ether, and its suspension in ether was then saturated with ammonia. The precipitate was washed with 5% caustic soda solution and with water, and was then dried and recrystallized from alcohol, when 0.35 g (7.8%) of 6-hexyl-3-phenylhydrouracil, m.p. 209-210°, separated (a mixture with a sample from the preceding experiment melted at 210°). Dilution of the alcoholic mother liquor with water yielded 3.2 g (70%) of 3-(3-phenylureido)nonanamide, m.p. 158° (fine colorless needles from aqueous alcohol).

Found %: N 14.40; 14.53
$C_{16}H_{25}O_2N_3$. Calculated %: N 14.43

Preparation of 3-Ureidononanamide. The reaction conditions were the same as those of the preceding experiment, 9.7 g of the ureido acid and 3.5 ml of thionyl chloride being taken. In order to separate the amide from the hydrouracil, the product was treated with 12% hydrochloric acid: 0.42 g of 6-hexylhydrouracil, m.p. 187°, was obtained [1] (a mixture with a sample from the previous preparation melted at 187°). Addition of 40% caustic potash solution to the cooled hydrochloric acid solution gave 7.05 g (72%) of the amide, m.p. 198° (fine colorless needles from water).

Found %: C 56.10; H 9.56; N 19.30; 19.28
$C_{10}H_{21}O_2N_3$. Calculated %: C 55.81; H 9.72; N 19.53

Action of Hypobromite on 3-Ureidononanamide. The amide (10 g) was added in small portions to a stirred hypobromite solution cooled to a temperature of −5° to −10° (5.83 g of bromine in 160 ml of 12.8% caustic potash solution). After three hours the solution was warmed to 50°, when a spontaneous rise in temperature occurred with vigorous gas evolution and the precipitation of an oil. When the solution attained 65°, it was cooled and extracted with ether. At the boundary between the ether and the alkali solution there was an intermediate layer, from which an amorphous acid (decomposition temperature 127-160°) separated on acidification.

Found %: C 55.93; 56.34; H 8.37; 8.29; N 18.10; 18.04
$C_9H_{18}O_2N_2$. Calculated %: C 56.40; H 8.22; N 18.40

Acidification of the alkaline solution gave 0.36 g of 3-ureidononanoic acid, m.p. 127-128°, and 0.27 g of 6-hexylhydrouracil, m.p. 186-187° [1]. The ether solution gave a neutral, partially crystallizing oil, from which, by treatment with hot water, 1.61 g of 1-carbamoyl-5-hexyl-2-imidazolidinone, m.p. 121°, was obtained (colorless prismatic plates from water).

Found %: C 58.24; 58.96; H 8.22; 8.37; N 19.89; 19.74
$C_{11}H_{21}O_2N_3$. Calculated %: C 58.34; H 8.89; N 19.71

Found: M 219.8; 221 (in dioxane)
Calculated: M 212.9

$C_{11}H_{21}O_2N_3$. Calculated %: C 58.87; H 8.05; N 19.90; M 211

Estimation of active hydrogen atoms: 2.02 (in ether-pyridine); 1.89 (in ether).

Hydrolysis of 1-Carbamoyl-5-hexyl-2-imidazolidinone. When the substance was boiled for 30 hours with 10% caustic soda, the previously described 4-hexyl-2-imidazolidinone [1], m.p. 119°, was obtained, and when it was boiled for 20 hours with concentrated hydrochloric acid the previously described 1,2-octanediamine was obtained and was identified as its bisethoxycarbonyl derivative, m.p. 98° [2].

SUMMARY

1. The preparation of β-ureido acids from amides of β-(alkoxycarbonylamino) acids has been extended to alkylamides and arylamides. 3-(3-Methylureido)- and 3-(3-phenylureido)-nonanoic acids were prepared in 70-75% yield. A method of preparing amides of β-ureido acids was developed.

2. By reaction of 3-ureidononanamide with hypobromite, a neutral compound was obtained, which was shown to be 1-carbamoyl-5-hexyl-2-imidazolidinone.

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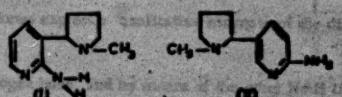
INVESTIGATION OF HYDROGEN BONDING IN α-AMINONICOTINE BY THE METHOD OF COMPARING INFRARED ABSORPTION SPECTRA

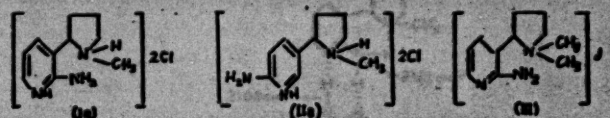
Ya. L. Goldfarb, M. S. Kondakova, and D. N. Shigorin

As Goldfarb and Kondakova [1] have shown, the amino derivatives of nicotine (I) and (II)—α-aminonicotine [2-amino-3-(1-methyl-2-pyrrolidinyl)pyridine] and α'-aminonicotine [2-amino-5-(1-methyl-2-pyrrolidinyl) pyridine]—behave differently toward alkyl halides. In explanation of this difference, they suggested that, in α-aminonicotine (I), the spatial proximity of the amino group to the pyrrolidine ring makes it possible for intramolecular hydrogen bonding to occur, so that the reactivity of the pyrrolidine nitrogen of (I) is lowered.



(I) (II)

In order to determine whether this suggestion is in accord with actual behavior, we decided to compare the infrared absorption spectra of the bases (I) and (II) themselves and also of their salts (Ia), (IIa), and (III)*:



(Ia) (IIa) (III)

It would be expected that, if intramolecular hydrogen bonding occurs in α-aminonicotine (I), its spectrum will differ from those of its salts (Ia) and (III), in which the quadricovalent pyrrolidine nitrogen atom cannot form such a bond; and it would be expected also that there would be no great difference between the spectra of the salts (Ia) and (IIa). The presence of a hydrogen bond in the base (I) may be detected also when its spectrum is compared with that of α'-aminonicotine, in which such a bond cannot arise.

The results of measurements of the infrared spectra of these compounds in the NH_2-frequency region are given in Table 1. The synthesis and purification of these compounds, and the method of measurement have been given previously [2, 3, 5].

As will be seen from Table 1, the NH_2 group in crystalline α-aminonicotine is characterized by two bands, whereas it has four bands in the spectrum of crystalline α'-aminonicotine. The reduction of the number of bands of the first compound from four to two can be explained by the deformation of the group arising from the formation of an intramolecular hydrogen bond.

Similar phenomena are observed in the infrared absorption spectra of 1-aminoanthraquinones and o-amino azo compounds [6, 7].

The assignment of the wave numbers can be made as follows. The NH_2 group of crystalline α-aminonicotine participates, by means of one of its N–H links characterized by the wave number 3325 (10) cm^{-1}, in the formation

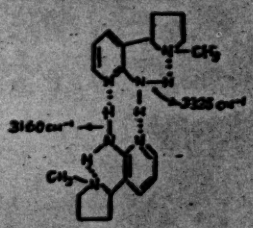
* The structures of the dihydrochlorides (Ia) and (IIa) as compounds arising by the addition of two protons to two ring nitrogen atoms, and of salt (III) as a pyrrolidinium iodide, were established previously [2–4].

TABLE 1

No.	Substance	Wave numbers for N—H bonds* (cm^{-1})
1	2-Aminopyridine (cryst.)	3448 (10, d), 3306 (5, d) 3170 (3, d)
2	α'-Aminonicotine (II) (cryst.)	3412 (10), 3315 (5), 3190 (4), 3130 (4)
	Solution in dioxane (1:20)	3480 (6), 3367 (10), 3222 (4)
	Solution in CCl_4 (1:20)	3485 (10), 3400 (5), 3320 (3), 3187 (1)
	Solution in CCl_4 (1:200)	3490 (8), 3400 (10), 3320 (2), 3185 (1)
3	α-Aminonicotine (I) (cryst.)	3325 (10), 3160 (5)
	Solution in dioxane (1:20)	3415 (10), 3290 (10), 3178 (1)
	Solution in CCl_4 (1:20)	3480 (10), 3290 (10, d) 3165 (3)
	Solution in CCl_4 (1:200)	3458 (8), 3292 (10, d) 3172 (1)
4	α-Aminonicotine methiodide (III) (cryst.)	3405 (5), 3310 (10), 3205 (3)
5	α-Aminonicotine dihydrochloride (Ia) (cryst.)	3425 (5), 3310 (3), 3180 (3), 3125 (2), 2560 (4) — diffuse band .... HCl
6	α'-Aminonicotine dihydrochloride (IIa) (cryst.)	3425 (10), 3345 (10), 3250 (10), 3110 (2), 2520 (3) — diffuse band .... HCl

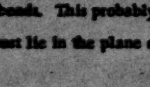
* The numbers in parentheses express a qualitative estimate of the differential intensities of the bands; d denotes diffusion.

of an intramolecular hydrogen bond, and by means of the other N—H link — wave number 3160 (5) cm^{-1} — it participates also in an intermolecular, probably "twinning", hydrogen bond:



Such an association between α-aminonicotine molecules is most probable in the crystal. The band for the valency vibration of the N—H link at wave number 3160 cm^{-1} in the crystal has a considerable intensity and almost coincides with the wave number of the valency vibration of the N—H link in 2-aminopyridine*. In the latter compound the occurrence of intermolecular association has been established by cryoscopic measurements [5]. The correctness of this assignment of wave numbers is supported by the fact that with reduction in the concentration of a solution of α-aminonicotine in carbon tetrachloride the intensity of the 3160 cm^{-1} band sharply diminishes (see Table 1); and in dioxane, in which the double molecule is probably broken down, this band is almost completely absent. The formation of monomer by dilution is also evidenced by the appearance of a new band at 3480 cm^{-1}, which is not observed in the spectrum of the crystal and is probably to be assigned to the valency vibration of an N—H bond that does not take part in hydrogen-bond formation.

Cryoscopic measurements on benzene solutions of α-aminonicotine (see Table 2) indicate that only in comparatively concentrated solutions (about 1:19) are some of the molecules of this base associated by means of intermolecular hydrogen bonds. This probably results from the fact that the intramolecular hydrogen bond



must lie in the plane of the pyrrolidine and pyridine rings, so that the second N—H link

of the NH_2 group, which could participate in the intermolecular bond, must lie outside this plane, which will hinder the formation of a double molecule, which also requires the arrangement of the participating groups in one

* Analysis of the infrared absorption spectrum of the NH_2 group of this compound is given in the paper [3].

TABLE 2

α-Aminonicotine		α'-Aminonicotine	
Proportions of α-aminonicotine and benzene (by weight)	Molecular weight	Proportions of α'-aminonicotine and benzene (by weight	Molecular weight
1:100	180	1:105.6	175
		1:108	187
1:80.3	182	1:85	207
1:49.7	190	1:53.2	218
1:34.9	202	1:42.5	224
1:31	197	1:32.7	229
1:27.3	204	1:31.0	233
1:20.5	208	1:22.9	244
1:19.3	210	1:20	247

plane. Hence, intra- and inter-molecular hydrogen bonds are competing together. It must be supposed that, in the case under consideration, the first of these two types of bonds is the stronger, for the formation of such a bond results in the formation of an energetically favorable six-membered ring. On this account this type of bonding is preserved in solution.

The α-aminonicotine band at 3325 cm^{-1} is displaced only slightly toward the longer waves (to 3290 cm^{-1}) in the carbon tetrachloride solution; its intensity is almost independent of the concentration of the solution and its diffuse character is preserved; these peculiarities are characteristic for the presence of an intramolecular hydrogen bond [8-12]. Here it must be stated that, as already noted above, the spectrum of α'-aminonicotine, in which intramolecular hydrogen bonding is excluded, differs substantially from that of α-aminonicotine and is very close in character to that of 2-aminopyridine. In this case there is a band at about 3185 cm^{-1}, which, judging by its closeness to the 3180 cm^{-1} band of the α-isomer and the fact that its intensity is reduced by dilution of the carbon tetrachloride solution, must be assigned to an N—H link participating in a "twinning" bond. The high wave numbers, 3485 and 3400 cm^{-1}, in solutions characterize the antisymmetrical and symmetrical vibrations of the free NH_2 group, respectively, and the bands at 3315, 3320, and 3222 cm^{-1} probably correspond to the overtone of the deformational band. The band at 3412(10) cm^{-1} in crystalline α'-aminonicotine probably corresponds to the valency vibration of the N—H links concerned in the weaker interaction between the twinned double molecules, which results in the formation of larger aggregates.

The cryoscopic measurements on benzene solutions of α'-aminonicotine are in accord with the infrared absorption spectra of this substance. These measurements, as also the spectra, show the close resemblance in behavior between α'-aminonicotine and 2-aminopyridine, and the substantial difference in behavior between these compounds and α-aminonicotine. The infrared absorption spectra and the cryoscopic measurements show that the intermolecular bonding in solution is stronger for α'-aminonicotine than for α-aminonicotine. This may be explained by the competing effect of intramolecular hydrogen bonding in α-aminonicotine and the absence of this effect in α'-aminonicotine.

The question of hydrogen bonding in α-aminonicotine is resolved still more clearly when its spectra are compared with those of the corresponding pyrrolidinium iodide (III). As would be expected, the addition of methyl iodide to the pyrrolidine nitrogen of the base (I), which renders the maintenance of the intramolecular hydrogen bond impossible, results in a return to a system containing a "normal", undeformed group, so that the compound is spectally almost indistinguishable from 2-aminopyridine in the region of N—H frequencies. We here find coincidence both in number of bands and in frequencies.

In α-aminonicotine dihydrochloride (Ia), as in the methiodide (III), the amino group cannot take part in an intramolecular hydrogen bond. In a comparison of the spectra of this salt (Ia) and the original base (I), we therefore find a change in the N—H bands, both in their number and in their frequencies. On the other hand, in a comparison of the absorption of the N—H region for α'-aminonicotine and its dihydrochloride, no essential difference is to be noted (see Table 1) — nor, indeed, is there any essential difference between the spectra of the dihydrochlorides of the two isomeric bases. All of this is in complete accord with the concept of the presence of an intramolecular bond in α-aminonicotine.

SUMMARY

Investigation of aminonicotines and their hydrochlorides by the method of infrared absorption spectra showed:

1. The presence of an intramolecular hydrogen bond in α-aminonicotine. The wave number for the valency vibration of the N—H link participating in the intramolecular hydrogen bond is 3325 cm^{-1} in the crystal and 3290 cm^{-1} in carbon tetrachloride solution.

2. The intramolecular bond in α-aminonicotine is broken when hydrogen halide or methyl iodide adds to the pyrrolidine nitrogen.

3. The hydrochlorides of α- and α'-aminonicotines have similar spectra.

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COMPOSITION OF THE THIOPHENE-GROUP COMPONENT OF THE GASEOUS PRODUCTS OF THE THERMAL DECOMPOSITION OF KASHPIR SHALES

Ya. L. Goldfarb, G. I. Gorushkina, and B. P. Fedorov

In the thermal decomposition of shales under the conditions applying at the Kashpir shale distillery, the products are: tar, containing, in particular, compounds of the thiophene series; semicoke; and gaseous decomposition products. The relatively high calorific value of this gas enables it to be used as furnace fuel. As the initial boiling temperature of Kashpir shale tar is about 125-127°, it is quite natural to suppose that much of the thiophene and its close homologs remain in the gas and are burnt in the furnaces. In order to determine the total content of these compounds in the products of the thermal decomposition of Kashpir shales*, we decided to separate the organic component (gas gasoline) from the so-called returned gas passing to the furnace burners and determine the individual and quantitative composition of the thiophene-group component**. With this object, we studied some samples of gas gasoline obtained at the Kashpir works by washing the returned gas from the retort furnaces with oil in a scrubber filled with Raschig rings. The shale-gas gasoline, separated from the oil absorbent by steam distillation, is a dark-brown liquid of unpleasant odor, boiling over the range of 40-200°, approximately. In Table 1 we give the characteristics of one of the several samples of gas gasoline that we investigated.

TABLE 1

Name of gasoline	d_4^{20}	Content of paraffins and cycloparaffins (%)	Engler fractionation					Found (%)		
			beginning of boiling (°C)	up to 100° (%)	up to 120° (%)	up to 150° (%)	up to 170° (%)	C	H	S
Gas gasoline	0.853	11.1	80	5	44	86	95	76.43	10.16	10.08

EXPERIMENTAL

In order to facilitate the solution of our problem, it was necessary to simplify the composition of the sample under investigation by suitable preliminary treatment, designed so that, as far as possible, the thiophene compounds and aromatic hydrocarbons remain unchanged in nature and amount. With this object a sample of the gas gasoline under examination was subjected to chemical purification: it was given two or three treatments with 78-79% sulfuric acid (10% by volume on amount of gasoline; 15 minutes; 2-3°), one or two treatments with 10% caustic soda (50% by volume on the amount of gasoline; 18-20°), and a chromatographic-adsorption treatment. These treatments resulted in the removal from the shale-gas gasoline of organic bases, partially unsaturated and readily polymerizable substances, and certain classes of oxygen- and sulfur-containing compounds, with the exception of thiophene and its homologs [1].

The chemical purification of shale oils rich in sulfur compounds first began to be discussed in the literature [2-4] in connection with the identification of the sulfur compounds present in shale oils and the development of a method of manufacturing ichthammol. Picon [1], who gives no experimental data, states that at below 30° 70% sulfuric acid has no action on thiophene and its homologs. We examined the behavior of thiophene and 2-methylthiophene, and of their solutions in benzene, toward 78-79% sulfuric acid, and we confirmed that no appreciable changes occur at 2-3° (Table 2).

There can be no doubt, however, that in such a treatment the thiophene compounds will to some extent be

* A later communication will deal with the composition of the thiophene-group component of the light fraction from the tar.

** In undertaking this work, the authors limited their task to the determination of the identities and contents of only those thiophene compounds that are present in more or less significant amounts in the products of the thermal treatment of Kashpir shales, including the gas gasoline.

removed mechanically by the acid, and that thiophenes may also be alkylated by olefins that are present and may react with aldehydes.

TABLE 2

Amount taken (ml)				Temperature of mixing and shaking (°C)	Time (minutes)	Amount obtained (ml)		
Benzene	Thiophene	2-Methylthiophene	78.7% H_2SO_4			Benzene or thiophene	Benzene + thiophene or 2-methyl-thiophene	H_2SO_4
50	—	—	5	2	15	49.8	—	5.1
—	5.8	—	0.6	3	15	5.6	—	0.6
—	5.4	—	0.6	2-3	15	5.5	—	0.5
5	5	—	1.0	2-3	15	—	9.9	1.1
5	10	—	1.5	3	15	—	15.0	1.5
45	—	5	5	2	15	—	49.8	5.0

TABLE 3

Gasoline	Amount obtained from 100 ml of original	d_4^{20}	n_D^{20}	Amount of paraffins and cycloparaffins (%)	Found (%)		
					C	H	S
Gas gasoline, chemically purified and distilled	58	0.841	1.4690	17.8	80.76	19.93	0.89

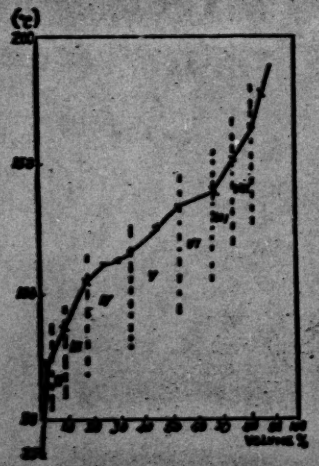

Fig. 1. Fractionation curve for purified gas gasoline before chromatographic treatment.

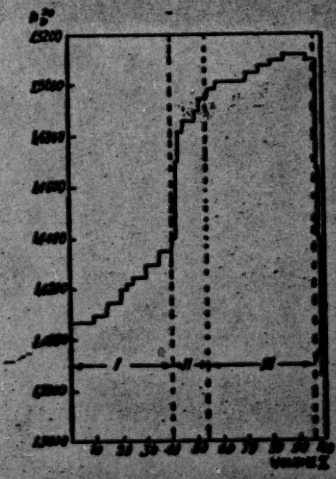

Fig. 2. Chromatogram of chemically purified gas gasoline.

Since, in our investigation, we were interested only in that part of the gas gasoline boiling below 200°, after purification and drying over calcium chloride the gas gasoline was generally distilled through a column at atmospheric pressure up to a temperature of 120°, and was then distilled up to the same temperature at a residual

pressure of 8-12 mm. Table 3 gives some of the characteristics of one of the chemically purified samples of gas gasoline.

We have shown that, when the object of investigation is the isolation of individual compounds from a gas gasoline or a shale-tar fraction and their quantitative estimation, chemical purification must be followed by chromatographic separation. The results on the individual composition of the thiophene fraction of shale tar published before this method of separation had acquired its present importance were obtained as the result of the treatment of large amounts of original material, and they are not always altogether convincing [2, 3]. When the chromatography stage is omitted and the shale-gas gasoline is fractionated through a column of 25-30 theoretical plates at a reflux ratio of 15-24, it is not possible to separate fractions boiling over narrow temperature ranges. Fig. 1 shows the fractionation curve for gas gasoline that has not been treated by chromatography. On this curve there is not a single clearly defined horizontal section, whereas there are several such sections on the fractionation curve (Fig. 3) for the same gasoline after chromatographic purification.

The difference in the distillation of gas gasoline before and after chromatographic treatment is to be explained by the fact that aromatic hydrocarbons and their thiophene analogs form azeotropic mixtures with certain saturated hydrocarbons [5]. This is confirmed by the group composition of chromatographed gas gasoline (concentrate of thiophenes and aromatics), which, as can be seen from Table 5, does not contain paraffins and cycloparaffins.

TABLE 4

B.p. of fraction (°C)	Gas gasoline after chemical purification			Gas gasoline after chemical purification and chromatography (thiophenes-aromatics concentrate)		
	Amount (%)	S (in %)	n_D^{20}	Amount (%)	S (in %)	n_D^{20}
Up to 78	4.8	3.04	1.4200	1.0	Nil	—
78-85	3.8	8.85	1.4670	5.7	8.9	1.4990
85-109	11.0	4.06	1.4360	Almost nil	—	—
109-114	17.1	12.65	1.4800	31.2	15.8	1.5080
114-133	18.5	7.87	1.4515	Almost nil	—	—
133-138	12.2	11.78	1.4830	32.6	20.2	1.5072
138-156	10.3	6.52	1.4590	10.0	Not determined	—
156-163	4.5	9.15	1.4750	8.6	18.6	1.5080

The distribution of sulfur content among the various fractions is also to be explained by the formation of azeotropic mixtures. As will be seen from the analytical data given in Table 4, in the gas gasoline that was only chemically purified, sulfur-containing compounds are distributed over all of the fractions, whereas in the gas gasoline that was treated chromatographically on silica gel almost 80% of the thiophene compounds were concentrated in four fractions.

Hence, by the use of chromatographic adsorption on silica gel, gas gasoline can be completely freed from paraffins and cycloparaffins and can be partially freed from unsaturated hydrocarbons, as a result, losses of the thiophenes and aromatics due to the formation of azeotropic mixtures are avoided. Moreover, this method makes it possible to obtain a thiophenes-aromatics concentrate that is free from nonthiophene sulfur-containing compounds [6, 7]. In the chromatographic treatment of gas gasoline we followed the directions given in Soviet and foreign literature [8]. The chromatography* was carried out in a column provided with a cooling jacket, and the adsorbent was activated silica gel. For 50 ml of chemically purified gas gasoline or light tar fraction we took 150 g of silica gel. Ethanol (140-150 ml) was used as eluant. The eluate was collected in three or four parts, depending on the values found for the refractive indices; in the present investigation the important part of the eluate was that leaving the column at n_D^{20} = 1.4900-1.5120, since this contained mainly thiophenes and aromatic hydrocarbons. The yield of this part of the eluate, which we refer to as the thiophenes-aromatics concentrate, was 41-42% by volume with a sulfur content of 16-17%.

The chromatogram is given in Fig. 2, and some of the characteristics of the thiophenes-aromatics concentrate are given in Table 5.

* The chromatography was carried out with the collaboration of Ya. L. Danyushevsky. It will be described in a future communication.

Fig. 3. Fractionation curve for purified gas gasoline after chromatographic treatment.

Investigation of the thiophenes-aromatics concentrate was continued by fractionating it through a column of the usual type having an efficiency of 26-30 theoretical plates [9]. The fractions collected were 78-85°, 109-115°, 134-136°, and 156-163°, corresponding, respectively, to the boiling points of thiophene, methylthiophene, dimethylthiophene, and ethylmethylthiophene. The results of the fractionation are given in Table 6 and Fig. 3.

Apart from aromatic hydrocarbons and thiophene compounds, these fractions contained only unsaturated hydrocarbons (Table 6).

The closeness between the chemical properties of thiophene and its homologs and those of aromatic hydrocarbons, and also the possibility of the presence of different isomers of alkyl-substituted thiophenes, made the task of establishing the structure of individual compounds — even those contained in the narrow fractions characterized above — a very complicated one. For the solution of this problem we used both chemical and optical methods. The use of chemical methods of investigation was based on the ability of certain reagents to react preferentially with the thiophene components of the mixture. The selective reagents that we used were acetyl chloride in presence of stannic chloride [10], acetic anhydride in presence of iodine [11] or phosphoric acid [12], and mercuric acetate or chloride [13]. The resulting ketones and mercury derivatives of the thiophene series, being greatly different in physical and chemical properties from the accompanying aromatic hydrocarbons, can be almost quantitatively separated from the latter.

The derivatives of thiophene and its homologs, isolated from the corresponding fractions and then purified, were identified by comparison with compounds prepared synthetically from chemically pure thiophene and its homologs.

TABLE 5

Part of eluate	Amount of thiophenes-aromatics concentrate obtained from 100 ml of purified gasoline (ml)	n_D^{20} mean	d_4^{20}	Amount (%)	Composition (%)		
					Paraffins	Thiophenes	Aromatics + unsaturates
Thiophenes-aromatics concentrate n_D^{20} 1.4980-1.5120	41-42	1.5088	0.931	17.2	Nil	~60	~40

TABLE 6

Sample investigated	Amount obtained from 100 ml of thiophenes-aromatics concentrate (ml) over the range					S content (%)	d_4^{20}	n_D^{20}	Composition of fraction (%)	
	78-85°	109-114.5°	134-136°	156-163°	173-180°				Thiophene compounds*	Aromatics + unsaturates
Thiophenes-aromatics concentrate from gas gasoline of Kashpir shales	5.7	—	—	—	—	8.87	0.907	1.4990	23.2	76.7
	—	31.2	—	—	—	15.60	0.935	1.5060	48.2	51.8
	—	—	32.6	—	—	20.20	0.939	1.5072	70.0	30.0
	—	—	—	8.6	—	18.62	0.941	1.5050	74.0	26.0
	—	—	—	—	1.9	—	—	—	—	—

* The content of thiophenes in the separate fractions of the chromatographed gasoline was calculated from the analytical data for sulfur.

Isolation and Identification of Thiophene and Benzene

Methyl 2-Thienyl Ketone and Benzene. A mixture of 36.6 g of the 78-85° fraction, containing about 23.3% of thiophene, and 8.6 g of acetyl chloride was cooled to 0° and was stirred while 26.1 g of stannic chloride was added; stirring was then continued for one hour at room temperature. Water (50 ml) was added, the water layer was separated, and the organic layer was neutralized with 4% caustic soda solution. The reaction product was steam-distilled. In order to remove unsaturated compounds, the oily distillate was treated with 0.5% permanganate solution, and the excess of the oxidizing agent was reduced with sodium bisulfite in a weakly acid medium. The benzene layer was separated, washed with sodium carbonate solution and with water, diluted with ether, and dried with calcium chloride. In the distillation, two fractions were collected: b.p. 78-80° (atmospheric pressure), n_D^{20} 1.4996, yield 19 g (87.5%); and b.p. 86-87° (11 mm), n_D^{20} 1.5660 (the literature [14] gives n_D^{20} 1.5667), yield 10 g (80%). For identification of the benzene obtained from the 78-85° fraction, it was converted into m-dinitrobenzene, m.p. 89-90°, undepressed by admixture chemically pure m-dinitrobenzene.

Oxime of Methyl 2-Thienyl Ketone. A mixture of solutions of 4.6 g of the ketone (b.p. 86-87° (11 mm) isolated as above in 23 ml of alcohol, 5 g of hydroxylamine hydrochloride in 10 ml of water, and 4.1 g of caustic potash in 4 ml of water was heated in a water bath for three hours. When reaction was complete, the solution was cooled, and the precipitate present was filtered off and washed with a little alcohol. Water (30-40 ml) was added to the filtrate, and the oxime that precipitated on acidification with 10% sulfuric acid was filtered off, washed with water, and dried; yield 2.5 g. Two recrystallizations from alcohol gave 0.6 g of substance melting at 110-112°. For the oxime of methyl 2-thienyl ketone the literature [15] gives m.p. 112-113°.

Found %: C 51.79; 51.20; H 5.28; 5.00; S 22.70; 22.68

$C_4H_3SC(=N\cdot OH)\cdot CH_3$ Calculated %: C 51.06; H 4.96; S 22.70

A mixture of the substance with the oxime prepared from synthetic methyl 2-thienyl ketone melted at 110-112°.

Isolation and Identification of Toluene and 2-Methylthiophene

Methyl 5-Methyl-2-thienyl Ketone and Toluene. A mixture of 125.5 g of the 110-114.5° fraction, containing about 58% of methylthiophene, and 153 g of acetic anhydride was cooled with ice water and stirred while 14 g of orthophosphoric acid (sp. gr. 1.62) was added. The reaction mixture was then stirred at 100-110° for three hours. It should be noted that, when the temperature reaches 85°, spontaneous evolution of heat occurs and the temperature rises rapidly to 120°, so that it is necessary to cool the reaction mixture. When cool, the mixture was poured into 500 ml of ice water, neutralized with 10% sodium carbonate solution, and steam-distilled. The oily distillate was extracted with ether, dried with calcium chloride, and distilled, the following fractions being collected:

Fraction I, b.p. 100-110° (750 mm): n_D^{20} 1.4950; 33.2 g. After refractionation through a Widmer column: b.p. 109.5° (747 mm): n_D^{20} 1.4962; 25.4 g (50%).

Found %: C 91.53; 91.63; H 8.85; 8.82

$C_6H_5CH_3$ Calculated %: C 91.53; H 8.87

For the identification of the toluene isolated from the 110-114.5° fraction, it was converted into 2,4-dinitrotoluene, m.p. 68-69° (the literature [16] gives m.p. 70°). A mixture with synthetic 2,4-dinitrotoluene melted at 68-70°.

Fraction II, b.p. 84-91° (2-3 mm); n_D^{20} 1.5575; 73.6 g (88%). After refractionation: b.p. 104-105° (13 mm); n_D^{20} 1.5602. After freezing out (the melting point of the ketone is 27°) and distillation at 103-104° (10 mm) the value of n_D^{20} was 1.5610 (the literature [17] gives n_D^{20} 1.5620).

Found %: C 69.83; 69.95; H 5.92; 5.97; S 22.08; 22.98

$C_4H_2(CH_3)COCH_3$ Calculated %: C 69.00; H 5.71; S 22.85

Oxime of Methyl 5-Methyl-2-thienyl Ketone. From 30 g of the ketone, b.p. 84-91° (2 mm), 27 g of the oxime, m.p. 103-119°, was prepared by the method described above. After recrystallization from alcohol: m.p. 126-127° (the literature gives 124-125.5° [15], 128° [18]).

Found %: C 54.39; 54.40; H 5.73; 5.86; S 20.64

$C_6H_2S(CH_3)C(=N\cdot OH)CH_3$. Calculated %: C 54.19; H 5.81; S 20.64

A mixture with the oxime prepared from synthetic methyl 5-methyl-2-thienyl ketone melted at 128-127°.

Isolation of m-Xylene and 2,5-Dimethylthiophene

2,5-Dimethyl-3-thienyl Methyl Ketone and m-Xylene. A mixture of 60 g of the 134-138° fraction, containing about 70% of dimethylthiophene, and 29.4 g of acetyl chloride was cooled to 0° and stirred while dropwise addition was made of 97.6 g of stannic chloride, the temperature being maintained at about 0°. In order to complete the reaction, the mixture was stirred for a further two hours at room temperature. Water (100 ml) was added, and the xylene layer was separated, neutralized with a 4-5% caustic soda solution, and steam-distilled. The distillate was washed with sodium carbonate solution and with water, and was then extracted with ether. The ether extract was dried, ether was distilled off, and the residue was vacuum-distilled and gave the following fractions:

Fraction I, b.p. 33-105° (12-14 mm); n_D^{20} 1.5029. After redistillation through a column; b.p. 135-140.5 (736 mm); n_D^{20} 1.4992; yield 12.9 g. As sulfur was found in the xylene isolated, a second treatment with acetyl chloride and stannic chloride was necessary. From 2.7 g of the xylene, after suitable treatment and distillation at 751 mm, the following fractions were obtained: 1.1 g, b.p. 136-138°; 1.5 g, b.p. 138-141°, n_D^{20} 1.4963.

Analysis of xylene, b.p. 138-141°:

Found %: C 90.85; 90.69; H 9.34; 9.48

$C_6H_4(CH_3)_2$. Calculated %: C 90.56; H 9.44

According to Raman-spectrum analysis, which was carried out by M. L. Batuev, the main component of the product was m-xylene.

After two vacuum fractionations, Fraction II was collected: b.p. 103-104° (10-11 mm); n_D^{20} 1.5448; yield 40.6 g. For 2,5-dimethylthiophene, the value of n_D^{20} was found to be 1.5449 (the literature [19] gives 1.5452).

Oxime of 2,5-Dimethyl-3-thienyl Methyl Ketone. From 33 g of the ketone, b.p. 103-104° (10-11 mm), 31.9 g of the oxime was prepared by the method described above; after two crystallizations from alcohol it melted at 82-83° (the literature [19] gives 83° for the melting point of the oxime of 2,5-dimethyl-3-thienyl methyl ketone. A mixture of the oxime obtained (m.p. 82-83°) with the oxime of the ketone synthesized from 2,5-dimethylthiophene melted at 81.5-83°.

Found %: C 56.09; 56.51; H 6.47; 6.50; S 19.04; 18.95; N 8.28; 8.49

$C_4HS(:CH_2)_2C(NOH)CH_3$. Calculated %: C 56.70; H 6.50; S 18.92; N 8.29

Isolation and Identification of 2-Ethyl-5-methylthiophene

The question of the structures of thiophene compounds in the 156-163° fraction was complicated by the fact that this range corresponds to the boiling points of twelve isomers of composition $C_7H_{10}S$. Hence, limiting our task to the determination of the identity of the thiophene homolog forming the bulk of this fraction, we decided first to isolate it as a mercury derivative, and, having studied its composition, establish the number of side chains in this homolog. Since the fraction contained a certain amount of unsaturated hydrocarbons, which could react with mercury salts and so complicate our work, it was necessary to remove them from the fraction. With this object, a solution of 100 ml of the fraction (b.p. 156-163°) in 100 ml of ethanol was shaken with 1% potassium permanganate solution for 1-2 minutes at 10-15°. The excess of oxidizing agent was reduced with sodium bisulfite solution in an acid medium, and the upper layer was washed with 1% caustic soda solution and with water, and was then dried. Distillation gave 93.5 ml of a fraction boiling at 159-163° (763 mm) and containing 29.8% of sulfur.

Preparation of the Mercury Derivative from the Fraction of b.p. 159-163° (763 mm) [13]. Experiment 1.

Mercuric acetate (10 g) was dissolved in 400 ml of distilled water, and 2 ml of 67% acetic acid was added. The slight turbidity of the solution was removed by filtering it into a jar having a ground-in stopper, and 1.3 g of the fraction of b.p. 159-163° was added (1.3 g of the fraction contained about 1 g of alkylthiophenes of composition $C_7H_{10}S$). The mixture was shaken for four hours at room temperature (20-25°), and a white crystalline precipitate gradually formed. The mixture was set aside overnight at room temperature, and the heavy white precipitate was filtered off and washed, first with water and then with alcohol. The well pressed, still moist, finely crystalline

precipitate was removed from the filter, ground in a mortar with a little glacial acetic acid, filtered off, again washed with alcohol, and dried at 105-110°. The yield was 3.9 g.

Found %: Hg 62.84 (Adams' method [20])

$C_4S(CH_3)(C_2H_5)(HgOCOCH_3)_2$. Calculated %: Hg 62.36

Experiment 2. A filtered solution of 35 g of mercuric acetate in 870 ml of 69-70% acetic acid was stirred at 40-50° while 6 g of the 159-163° fraction (containing about 77% of compounds of formula $C_7H_{10}S$) was added. A white crystalline precipitate began to form after 6-7 minutes. The temperature was then raised to 60° and the mixture was stirred for three hours. On the next day the crystalline precipitate was filtered off, washed with warm water until the reaction was neutral, and then washed with alcohol. The yield was 19 g. Recrystallization of 5 g from 85 ml of glacial acetic acid gave 2.8 g of substance, which was dried at 105-110°. When heated rapidly in a capillary, the substance began to darken at 244-245° and melted with decomposition at 249-250°.

Found %: Hg 61.50; 62.30; C 20.35; 20.43; H 2.22; 2.34

$C_4S(CH_3)(C_2H_5)(HgOCOCH_3)_2$. Calculated %: Hg 62.36; C 20.52; H 2.19

Synthesis of 3,4-Bisacetoxymercuri-2-ethyl-5-methylthiophene from Synthetic 2-Ethyl-5-methylthiophene

2-Ethyl-5-methylthiophene. According to the literature [21], this thiophene homolog can be prepared in 40% yield by heating the semicarbazone of methyl 5-methyl-2-thienyl ketone with alkali. Using this method, we obtained only a 14% yield of 2-ethyl-5-methylthiophene (b.p. 158-160°; n_D^{22} 1.5073). We therefore decided to prepare it from the hydrazone of methyl 5-methyl-2-thienyl ketone [22]. A mixture of 35 g of methyl 5-methyl-2-thienyl ketone (n_D^{22} 1.5605), 200 ml of ethylene glycol (b.p. 195-197°), and 70 g of 85% hydrazine hydrate was prepared in a one-liter flask provided with a thermometer set with its bulb below the level of the liquid, a 24-cm fractionating column, and a condenser set for distillation. The reaction mixture was heated in an oil bath, the temperature being raised gradually over a period of 40 minutes to 160° (bath temperature 180°). Water and a little (about 1 g) of methyl 5-methyl-2-thienyl ketone distilled off. The liquid was cooled to 60°, 60 g of ground caustic potash was added, and heating was continued, the temperature being raised to 170°. At 130° vigorous evolution of nitrogen occurred and 2-ethyl-5-methylthiophene began to distil over. The ethylmethylthiophene was extracted with ether and the ether extract was washed — first with dilute (1:5) hydrochloric acid, then with sodium carbonate solution, and finally with water; it was dried with calcium chloride. The residue remaining after removal of ether was distilled at atmospheric pressure, and 26.3 g of a fraction of b.p. 158-159° (761 mm) was obtained. It had n_D^{22} 1.5073 (the literature [21, 22] gives n_D^{22} 1.5072).

3,4-Bisacetoxymercuri-2-ethyl-5-methylthiophene. Synthetic 2-ethyl-5-methylthiophene 2 g, b.p. 158-159° (761 mm), was added to a filtered solution of 5.1 g of mercuric acetate in 50 ml of 67% acetic acid. The resulting solution was shaken at 32-40° for two hours; a white crystalline precipitate began to appear after 10-15 minutes. On the next day the precipitate was filtered off and washed — first with 70% acetic acid, then with hot water, and finally with alcohol. The yield was 4.1 g (40%). Recrystallization from glacial acetic acid gave snow-white crystals (2 g) of the mercury derivative; they were filtered off and washed with glacial acetic acid and with alcohol.

Found %: Hg 62.43

$C_4S(CH_3)(C_2H_5)(HgOCOCH_3)_2$. Calculated %: Hg 62.36

Synthetic 3,4-bisacetoxymercuri-2-ethyl-5-methylthiophene, the same substance obtained from the 159-163° fraction, and a mixture of these two preparations were heated separately in capillaries at the rate of 9° per minute, and in each case the substance began to darken at 244-245°, and then melted with formation of glistening black specks at 249-250°. No further change occurred when the capillaries were heated to 280° in a sulfuric acid bath.

Identification of 2-Ethyl-5-methylthiophene in the Form of 3,4-Dibromo-2-ethyl-5-methylthiophene 1,1-Dioxide

Preparation of 3,4-Dibromo-2-ethyl-5-methylthiophene from Synthetic 2-Ethyl-5-methylthiophene. A solution of 36.7 g (11.7 ml) of bromine in 25 ml of carbon disulfide was added at room temperature over a period of 90 minutes to a solution of 12.6 g of 2-ethyl-5-methylthiophene in 20 ml of carbon disulfide. The solution was boiled for 10-15 minutes, and 3 g of cuprous cyanide was then added [23]. Carbon disulfide was removed at the pump, and the residue was boiled for 15 minutes with a solution of 4 g of caustic potash in 20 ml of alcohol. The reaction mixture was

diluted with water, acidified with hydrochloric acid, and steam-distilled. The product was 16.2 g (44.5%) of a faintly yellowish oil. It was dried and vacuum-distilled, when it gave 12.8 g of substance of b.p. 118-121° (7-8 mm) and n_D^{20} 1.5904. After being redistilled the substance had b.p. 119-121° (7-8 mm) and n_D^{20} 1.5898.

Found %: C 29.98; H 2.85

$C_4S(CH_3)(C_2H_5)Br_2$. Calculated %: C 29.60; H 2.82

3,4-Dibromo-2-ethyl-5-methylthiophene 1,1-Dioxide. 3,4-Dibromo-2-ethyl-5-methylthiophene (2.9 g) was dissolved in 26 ml of glacial acetic acid, and 4 ml of 30% hydrogen peroxide was added. The mixture was heated with stirring at 60-80° for 30 minutes and at 78-81° for five hours, after which it was poured in 200 ml of water. The reaction product was shaken twice with 75 ml of ether, the ether extract was dried with calcium chloride, and the ether was distilled off. The residual thick reddish-brown oil did not crystallize after being cooled and was allowed to stand for 36 hours. However, after the addition of 5-6 ml of dry methanol to the oil, a white crystalline precipitate of the dioxide began to form, and the amount of this increased appreciably when the mass was cooled to −1°. The dioxide was filtered off and washed with a little methanol (0.55 g of crystals, m.p. 55-56°).

The oil remaining after evaporation of the alcohol was again treated with 2 ml of hydrogen peroxide in glacial acetic acid at 60-75° for 12 hours, the further treatment being as described above. A further 0.70 g of the dioxide, m.p. 54-58°, was obtained, the total yield being 1.25 g (about 40%). After being recrystallized from methanol, the dioxide melted at 61-62°; further recrystallization did not affect the melting point.

Found %: C 26.70; 26.76; H 2.45; 2.42

$C_4SO_2(CH_3)(C_2H_5)Br_2$. Calculated %: C 26.59; H 2.55

Preparation of 3,4-Dibromo-2-ethyl-5-methylthiophene from the Fraction of b.p. 156-163°. The 156-163° fraction (42 ml) was first given a preliminary treatment with 2% potassium permanganate solution (two portions of 150 ml) in order to remove unsaturated hydrocarbons. Excess of oxidizing agent was reduced with sodium bisulfite in an acid medium, and the oil was then washed three times with water, twice with 1% caustic soda solution, and twice with water again. It was then dried with calcium chloride and distilled at 159-163°. The resulting fraction, amounting to 31.2 g, contained 17.6% of sulfur (equivalent to about 70% of 2-ethyl-5-methylthiophene). It was dissolved in 35 ml of carbon disulfide, and the solution was stirred for 75 minutes while a solution of 20 ml of bromine in 50 ml of carbon disulfide was added. Further treatment (see the experiment on the bromination of synthetic ethylmethylthiophene) gave 36.5 g of an oil. This was vacuum-fractionated, and the following three fractions were collected.

Fraction I, b.p. 45-100° (7-8 mm): 6.5 g; n_D^{20} 1.5025
Fraction II, b.p. 100-122° (7-8 mm); 7.4 g; n_D^{20} 1.5738
Fraction III, b.p. 122-124° (7-8 mm); 17.5 g; n_D^{20} 1.5880

Fractions II and III were combined and redistilled. The distillate collected (16 g) had b.p. 118-121° (7-8 mm) and n_D^{20} 1.5880.

Found %: C 30.08; 30.08; H 2.89; 2.83

$C_4S(CH_3)(C_2H_5)Br_2$. Calculated %: C 29.60; H 2.82

Preparation of 3,4-Dibromo-2-ethyl-5-methylthiophene 1,1-Dioxide from the Fraction of b.p. 159-163°. A solution of 2.9 g of the bibromo derivative (see preceding experiment) in 25 ml of acetic acid was warmed to 60° and was stirred while 6 ml of 30% hydrogen peroxide was added over a period of 26 hours, the temperature being raised gradually from 60° to 72°. The solution was then poured into 250 g of pounded ice, and a finely crystalline colorless substance was immediately precipitated together with a little oil. On the next day the mixture was cooled to 2-3° and filtered. The crystals were washed with water (1.65 g, m.p. 51-56°). Recrystallization from 8 ml of methanol gave 0.85 g of substance of m.p. 61-62.5°. In admixture with the synthetic dioxide it melted at 61-62.5°.

Found %: C 26.50; 26.31; H 2.47; 2.51

$C_4SO_2(CH_3)(C_2H_5)Br_2$. Calculated %: C 26.59; H 2.55

SUMMARY

It was shown that the main bulk of the light fraction of the thiophenes-aromatics part of Kashpir shale-gas gasoline consists of the following aromatic hydrocarbons and thiophene compounds: benzene, toluene, m-xylene, thiophene, 2-methylthiophene, 2,5-dimethylthiophene, and 2-ethyl-5-methylthiophene.

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HIGH-TEMPERATURE REACTIONS OF DECANE OVER PLATINIZED ALUMINA IN PRESENCE OF HYDROGEN AT HIGH PRESSURE

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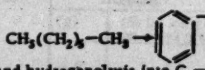
In a previous paper [1] we described an investigation of the contact-catalysis reactions of heptane in presence of platinum, palladium, rhodium, and ruthenium supported on silica gel at 460° and under 20 atm of hydrogen in a flow-type apparatus. A study of the catalysis products showed that, under these conditions, part of the heptane undergoes dehydrocyclization with formation of toluene:



and another part undergoes isomerization and hydrogenolysis into C_5-C_7 isoparaffins. It was found that the most active catalyst for the isomerization of heptane is platinized silica gel.

In the present investigation we have studied the reactions of decane in contact with platinized alumina at 460° under a hydrogen pressure of 30 or 50 atm in a flow system. Detailed investigation of the catalyzates showed that, under the given conditions, decane reacts in various directions. It was shown that the main products of these reactions are C_{10} isoparaffins, which are present in the catalyzate to the extent of 36-38% (depending on the pressure). The catalyzates were found to contain also isoparaffins of lower molecular weight, a small amount of aromatic hydrocarbons, and also some cyclopentanes and cyclohexanes.

The formation under these conditions of cyclopentanes and cyclohexanes is of particular interest. The presence of cyclopentane hydrocarbons in the catalyzates shows that they are formed not only at ordinary pressure over platinized charcoal of high platinum content (20%), as shown by Kazansky, Liberman, and coworkers [2, 3], but also under a pressure of hydrogen over platinized alumina containing only 1% of platinum. We consider that, within certain limits, the stabilizing effect of a pressure of hydrogen makes it easier to establish optimum conditions for the dehydrocyclization of alkanes with formation of cyclopentanes and to study the mechanism of this new reaction, for it is known [4] that increase in hydrogen pressure greatly reduces the tendency for the cyclopentane ring to open. Also, the results of the present work confirm that, as we have recently established [1], cyclohexane hydrocarbons are formed intermediately in the catalytic aromatization (dehydrocyclization) of alkanes.

Hence, the catalytic synthesis of cyclopentanes and cyclohexanes from alkanes occurs not only under the conditions of Zelinsky dehydrogenation catalysis, but also under considerably different conditions with respect to temperature, pressure, space velocity, and nature of catalyst.

EXPERIMENTAL

Synthesis of Decane. The Gringnard reaction between butyraldehyde and hexylmagnesium bromide yielded a secondary decanol, which was dehydrated over alumina at 320°. The dehydration product was suitably purified and then hydrogenated in the vapor phase at ordinary pressure in presence of platinized charcoal (1% Pt) at 210°. The resulting decane was treated with sulfuric acid, with sodium carbonate solution, and with water, and was distilled over sodium through a 36-plate column. The properties of the product were as follows: b.p. 173.5-174.5° (corrected); n_D^{20} 1.4120; d_4^{20} 0.7306; f.p. −29.5° to −30°; Found MR 48.45; Calculated MR for $C_{10}H_{22}$ 48.38. For decane the literature [5] gives the following properties: b.p. 174.11°; n_D^{20} 1.4118; d_4^{20} 0.7299; f.p. −29.67°.

Catalyst. The reactions studied were carried out in presence of platinized alumina (1% Pt), the preparation and properties of which we have described in a previous paper [6].

Experimental Conditions. The experiments were carried out at 460°. The decane was brought into contact with the catalyst at a space velocity of 1.1 hour^{-1}, the molar ratio of hydrogen to hydrocarbon being 5:1. Hydrogen pressures of 30 and 50 atm were used. The apparent volume of the catalyst was 50 ml. The apparatus and experimental arrangement were described in detail in a previous paper [1].

TABLE 1

Properties of Decane Catalyzates obtained in presence of 1% Pt on Al_2O_3

Pressure of H_2 (atm)	Amount of decane taken for reaction (g)	Amount of catalyzate (g)	Gas and losses (%)	Properties of catalyzate			Composition of gas (%)	
				n_D^{20}	d_4^{20}	Content of aromatic hydrocarbons (% by volume)	H_2	C_nH_{2n+2}
30	162.0	157.0	3.0	1.4155	0.7324	3.0	97.8	2.2
50	68.5	65.5	4.3	1.4125	0.7306	Traces	96.3	3.7

TABLE 2

Properties of Fractions Distilled from the Paraffin-Naphthene Part of the Catalyzate before its Treatment with Urea

Experiment No.	Boiling range of fraction (°C)	Amount		n_D^{20}	d_4^{20}	Aniline point (°C)
		(g)	(% by weight on catalyzate)			
1	52-100°	6.2	4.0	1.4025	0.7233	52.2
2	50-100°	4.1	6.2	1.3870	0.6793	

° In both cases the bulk of the hydrocarbons distilled at 65-100°.

TABLE 3

Properties of Hydrocarbons After Separation of n-Alkanes from Isoparaffins by means of Urea

Experiment No.	Properties of n-alkane-isoparaffin mixture before treatment with urea		Properties of isoparaffins separated from their mixture with n-alkanes		Properties of n-alkanes entering into the complex with urea	
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}
1	1.4130	0.7332	1.4137	0.7405	1.4120	0.7314
2	1.4137	0.7346	1.4150	0.7410	1.4120	0.7298

Investigation of the Catalyzates. Liquid catalyzates were characterized by density, refractive index, and content of aromatic hydrocarbons. The latter were separated from the naphthene-paraffin part of the catalyzate by chromatographic adsorption on silica gel [7]. The separation of n-alkanes from isoparaffins was effected by treatment of the mixture with urea. As cyclohexane was used as diluent in the treatment of the dearomatized part of the catalyzate with urea, hydrocarbons boiling up to 100° were first distilled from this part of the catalyzate through a 33-plate column. Hydrocarbons of the separate classes isolated in this way were identified by chemical and optical methods. Table 1 gives the properties of the catalyzates obtained by treatment of decane in presence of platinized alumina under the conditions stated above.

As will be seen from the data in Table 1, the properties of catalyzates obtained at different pressures do not differ essentially. However, when the pressure is raised from 30 to 50 atm, the content of aromatics in the catalyzate is appreciably reduced and the amount of saturated hydrocarbons in the gas is somewhat increased.

By adsorption on silica gel 4.6 g of aromatic hydrocarbons was separated from the decane catalyzate obtained at 30 atm. This fraction was distilled at 750 mm from a small flask provided with fractionating column; it had the following properties: b.p. 108-121° (the bulk came over at 108-114°), n_D^{20} 1.4955 and d_4^{20} 0.8630. Optical analysis of this fraction showed that it consisted of toluene together with a small amount of xylenes.

After the properties of the dearomatized part of the catalyzate has been determined, hydrocarbons boiling up to 100° were separated from it by distillation through a 33-plate column. The properties of these head fractions are given in Table 2.

The data given in Table 2 show that the properties of the hydrocarbons of the head fractions differ greatly, in spite of the closeness of the boiling limits. These fractions were subjected to optical analysis. Investigation of the first fraction, b.p. 52-100°, showed that it consisted of a mixture of cyclopentane hydrocarbons (mainly

TABLE 4

Fractional Composition and Properties of n-Alkanes Isolated from the Decane Catalyzate obtained in presence of $Pt-Al_2O_3$

Experiment No.	Weight of n-alkanes taken for fractionation (g)	Fraction No.	Boiling range (°C)	n_D^{20}	d_4^{20}	Amount (g)	Yield of fraction in % by weight on		
							mixture taken	catalyzate	original hydrocarbon
1	86.0	I	165-173	1.4125	0.7325	5.5	6.4	3.5	3.4
		II	173-174.5	1.4120	0.7304	77.1	90.0	49.1	47.6
		III	174.5-175.5	1.4120	0.7306	2.5	2.9	1.9	1.8
			Residue	—	—	0.3			
2	34.8	I	135-150	1.3875	0.7113	1.0	2.9	1.5	1.5
		II	150-172	1.4140	0.7307	2.5	7.2	3.8	3.8
		III	172-174.5	1.4125	0.7310	27.5	79.0	42.0	40.1
		IV	174.5-175.5	1.4125	0.7315	2.6	7.5	4.0	3.8
			Residue	—	—	0.4	—	—	—

TABLE 5

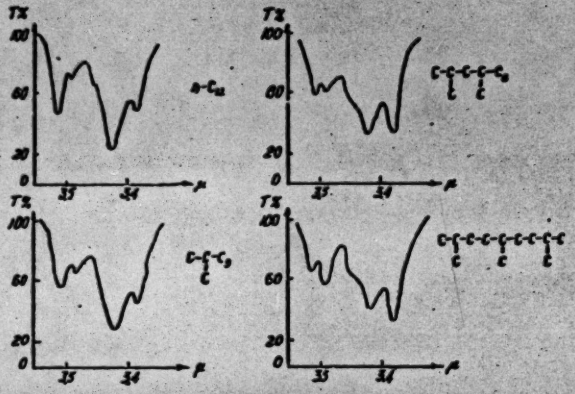
Fractional Composition and Properties of Isoparaffins Isolated from the Decane Catalyzate Obtained in Presence of $Pt-Al_2O_3$

Experiment No.	Weight of isoparaffins taken for fractionation (g)	Fraction No.	Boiling range (°C)	n_D^{20}	d_4^{20}	Amount (g)	Yield of fraction of % by weight on		
							mixture taken	catalyzate	original hydrocarbon
1	49.0	I	100-130	1.4105	0.7592	3.5	7.1	2.3	2.2
		II	130-155	1.4095	0.7315	7.8	16.0	5.0	4.8
		III	155-160	1.4130	0.7285	1.2	2.5	0.8	0.7
		IV	160-164	1.4140	0.7365	5.5	11.3	7.2	3.4
		V	164-167	1.4140	0.7315	11.8	24.1	8.2	7.3
		VI	167-170	1.4128	0.7352	17.0	34.7	11.0	10.5
		Residue	—	—	—	0.4			
2	20.3	I	100-130	1.4080	0.7479	1.7	8.4	2.6	2.5
		II	130-155	1.4095	0.7299	4.5	4.5	22.2	6.9
		III	155-160	1.4130	0.7285	0.5	2.5	0.8	0.7
		IV	160-164	1.4148	0.7365	2.3	10.8	3.4	3.2
		V	164-167	1.4142	0.7317	5.3	24.8	8.1	7.8
		VI	167-170	1.4128	0.7350	4.4	21.7	6.7	6.4
		Residue	—	—	—	0.3			

methylcyclopentane) and isoparaffins. Judging from its aniline point, this fraction contained 55% of cycloalkanes (the calculated value was 55.8%). The fraction isolated from the catalyzate obtained at 50 atm consisted mainly of 2- and 3-methylhexanes.

Separation of n-Alkanes and Isoparaffins with the aid of Urea. As is well known, the method of separating n-alkanes from isoparaffins with the aid of urea has been very extensively used during recent years [8, 9]. We made use of this method for the separation of the n-alkanes in the dearomatized catalyzates from their isomers. Table 3 gives the properties of hydrocarbons of normal and branched structures after their separation by means of urea.

Spectrum Analysis of Products of the Catalytic Treatment of Decane. It is known that molecular-spectrum analysis of mixtures of complex hydrocarbons of the kerosene range (C_8 and higher) is rendered difficult by a lack of hydrocarbon standards and by the weakness of the Raman lines. Hence, the comparatively wide boiling range of the fractions separated by distillation and the probability of their containing various C_{10} isomers made it impossible to expect satisfactory results in their analysis by the Raman-spectrum method.



Infrared spectra of C_{11} paraffins.

In order to estimate the extent of branching in the hydrocarbons that we obtained, we made use of the relationships found by one of us on the basis of a new assignment of wave numbers in the CH vibration region [10]. When we compare the infrared absorption in this region (2800-2979 cm^{-1}) for C_{11} paraffins differing in extent of branching (number of CH_3 groups), we obtain the graphical relationship shown in the figure. In the case of paraffins containing a different number of carbon atoms, the changes in the peaks will be analogous. As the number of CH_3 groups is increased, the greatest changes are observed in the peaks at 3.51; 3.42, and 3.38 μ; with increase in ramification, the first two peaks become regularly lower, and the third becomes higher. The first two peaks are associated with the number of CH_2 groups, and the third with the CH_3 groups. When all of the spectra are obtained under identical conditions, then from the values of the ratios of the absorption coefficients for the 3.51 and 3.38 μ peaks and for the 3.42 and 3.38 μ peaks, we may form a fairly close idea of the extent of branching in the hydrocarbon or hydrocarbon mixture. For this purpose we selected the following conditions: spectrometer, Infrared-11; slit, 0.2 mm; concentration of hydrocarbon in carbon tetrachloride, 1:50 by volume. Control experiments on artificial binary and ternary mixtures gave satisfactory results (error about 10%).

Since the fractions isolated from the isoparaffin part of the decane catalyzate in experiments at 30 and 50 atm (see Tables 4 and 5) differed comparatively little in properties, the like fractions were combined for spectroscopic investigation. The following results were obtained. The Raman spectrum was determined for Fraction I, b.p. 100-130°, and we succeeded in showing the presence of isoparaffins (probably C_9) in admixture with methylcyclohexane. In order to obtain more precise information, 3.4 ml of this fraction was subjected to dehydrogenational catalysis at 300° over platinized charcoal. The resulting catalyzate had n_D^{20} 1.4160 (the original fraction had n_D^{20} 1.4105). This catalyzate was sulfonated, and the sulfonic acid obtained was decomposed by Kizhner's method, when 0.3 g was obtained of a substance which, according to its ultraviolet spectrum, contained toluene. This result is in accord with the indications obtained from Raman spectra.

Fraction II, b.p. 130-155°, was a mixture of C_9 and C_{10} isoparaffins in which mono- and di-substituted alkanes were present in almost equal amounts. Fraction III, b.p. 155-160°, consisted of about 40% of C_{10} mono- and 60% of C_{10} di-substituted alkanes. Fraction IV, b.p. 160-164°, contained about 70% of C_{10} mono- and 30% of C_{10} di-substituted alkanes. Fraction V, b.p. 164-167°, consisted of C_{10} monosubstituted alkanes. Fraction VI, b.p. 167-170° contained about 75% of C_{10} monosubstituted alkanes and 25% of unchanged n-decane.

Thus the combined method, applied to the investigation of the decane catalyzate, enabled us to establish the presence of cyclopentane and cyclohexane hydrocarbons in this catalyzate.

SUMMARY

1. An investigation was made of the contact-catalysis reactions of decane at 460° in presence of platinized alumina in a flow system, hydrogen being present at a pressure of 30 or 50 atm.

2. It was shown that, under the conditions described, this hydrocarbon undergoes some far-reaching transformations: the reaction product was found to contain aromatic hydrocarbons, cyclopentane and cyclohexane hydrocarbons, and C_7-C_{10} mono- and di-substituted alkanes. C_{10} monosubstituted alkanes formed 70% of the total amount of C_{10} isomers present.

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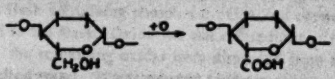
CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE BY OXIDIZING AGENTS

COMMUNICATION 9. OXIDATION OF CELLULOSE BY NITROGEN DIOXIDE

E. D. Kaverzneva, V. I. Ivanov, A. S. Salova, and S. A. Kist*

Shorygin and Khait [1] showed that, when cellulose is treated with gaseous nitrogen dioxide, practically no nitric ester groups are formed and the reaction product is completely soluble in hot sodium carbonate solution. According to their results, the action of oxides of nitrogen on cellulose differs markedly from that of other oxidizing agents, and makes it possible to introduce a large number of carboxyl groups into the fiber without affecting its appearance and strength. At the same time, the fiber acquires acidic properties and becomes readily soluble in alkalis. At first, therefore, this reaction was regarded as a specific oxidation of primary alcohol groups in the 6-positions of the glucose residues to COOH:



From 1942 onward the oxidation of cellulose by oxides of nitrogen was studied by Kenyon and coworkers, who published the first systematic work on this matter and patented this method of oxidation. They later investigated the quantitative determination of COOH groups in the resulting oxycelluloses [3], the solubility of the preparations in alkalis [4], and the possible mechanism of the reaction [5]. Their results were confirmed by Maurer and Reiff [6], who, by sufficiently prolonged oxidation, obtained preparations having COOH contents close to the value theoretically possible on the assumption that one alcohol group per glucose residue is oxidized (25.50%; theory requires 15.5%). Pfeiffer [7] investigated the effect of the conditions of oxidation and the properties of salts formed by the oxycelluloses with various metal cations. A result of these investigations was that the specificity originally assumed, almost unconditionally, for the oxidative action of nitrogen dioxide on carbohydrates (oxidation of only primary alcohol groups) began to be the subject of some doubt.

In his first papers, Kenyon explained some of the properties of celluloses oxidized by oxides of nitrogen, i.e. their high copper numbers and the readiness with which they are hydrolyzed in an alkaline medium, by the presence of a large number of electronegative COOH groups. This concept was clearly inadequate in view of the fact that alginic and pectic acids are completely stable to alkalis. Later, Kenyon, referring to our work [8], suggested that keto groups are formed in the course of the oxidation and that still other, not yet established, oxidative changes might occur. In recent work, Nevell [9] and Nabar and Padmanabhan [10] seek an explanation of the characteristic properties of these oxycelluloses in the supposed presence of various functional groups (keto, dialdehyde). According to Nevell's experiments, the amount of oxygen required in the formation of the oxidized preparations can be higher than two atoms per glucose residue, and the COOH content may exceed the theoretically possible value (he found 700 mmoles of COOH per 100 g of oxycellulose, instead of the calculated amount of 568 mmoles). Hence, in addition to the oxidation of primary alcohol groups, other oxidation reactions occur.

In spite of the considerable number of investigations that have been carried out, the mechanism of the oxidation of cellulose by oxides of nitrogen has not yet been studied and the identity of the chemical reactions occurring is far from clear. In most of the textbooks on wood and cellulose chemistry, e.g. "Wood Chemistry" (1952) by Hägglund, nitrogen dioxide is still classified as a specific oxidant.

* Deceased.

EXPERIMENTAL

The object of the present investigation was to obtain a more precise picture of the chemical changes undergone by cellulose when treated with oxides of nitrogen.

The experiments were carried out on purified bleached cotton cellulose taken in the form of gauze and cotton wool. Apparatus was set up for the preparation of nitrogen dioxide, its drying, and its distillation, and apparatus was set up also for carrying out the oxidation of the cellulose. The starting materials used for the preparation of nitrogen dioxide were nitric acid (sp-gr. 1.32-1.35) and technical ferrous sulfide. The oxidation of the resulting oxides was completed, and the product was dried over phosphoric oxide and distilled: b.p. 21.2-21.5°; yield 300-400 g from 1500 ml of nitric acid.

The oxidation of cellulose was carried out in a glass apparatus about 11 liters in volume; this was connected to a container for nitrogen oxides, which was provided with a reflux condenser. The excess gases were removed from the system through the condenser and an absorption vessel containing alkali. In most of the experiments some phosphoric oxide was introduced into the container for nitrogen oxides in order to bind the water formed, but complete removal of traces of water was not demanded by the experimental conditions, and the cellulose to be oxidized was taken in the air-dry condition.

Description of Experiments. The cellulose (50-100 g in the form of medicinal gauze or cotton wool) was placed in a large desiccator, which served as a reactor, and was supported by a glass stand or was wrapped on aluminum gauze. The necessary amount of nitrogen dioxide (generally 0.5-2.0 parts of NO_2 for each part of cellulose) was poured into a flask containing phosphoric oxide and connected by two tubes to the desiccator. A reflux condenser was attached to the flask. Oxidation was carried out at room temperature for 24-96 hours. When reaction was complete, the remaining oxides were displaced from the apparatus with dry air and the cellulose was transferred to cold distilled water. It was steeped in seven changes of water, and in the last, 60-minute steep the water acquired an acidity of not more than 0.003%, calculated as nitric acid. The oxycellulose was dried at not above 50°, since it yellowed at higher temperatures. The samples obtained were analyzed for moisture, ash, nitrogen, and functional groups, i.e. total [11] and uronic [12] carboxyls, aldehyde groups [13], and total carbonyl groups [14] by previously described methods, which have been partially modified by us [15]. In addition, carbonic ester groups [16], nitric ester nitrogen, and α-hydroxy ketone groupings were determined.

The methods that have been developed for the determination of functional groups in oxycelluloses required careful verification and considerable modification before they could be applied to oxycelluloses of the type under investigation. On account of the acidic properties of the the preparations, it was found to be essential to increase the acetate concentration in the determination of total carboxyls by the calcium acetate method so as to avoid excessive lowering of the pH of the solution. It was necessary also to increase the concentration of the borate buffer in the iodometric determination of aldehyde groups.

Qualitative Characterization of the Preparations Obtained. All of the preparations of cellulose oxidized with nitrogen dioxide were very acid, the pH of a water extract being 2.7-4.0. They gave positive reactions for lactone groups (with ferric chloride after condensation with hydroxylamine) and for enediol groups (Benedict's reagent). The reaction with potassium iodide for peroxide compounds was negative. The mechanical strength of the preparations was somewhat less than that of the original cellulose, and it fell appreciably as the samples were kept.

Functional Groups in Celluloses Oxidized with Nitrogen Dioxide

a) Nature of the Carboxyl Groups. As the analyses show, most of the carboxyls are uronic carboxyls and are therefore formed at C-6 (see Table 1).

TABLE 1

Nature of the Carboxyl Groups in Celluloses Oxidized with Nitrogen Dioxide

Experiment No.	Total COOH (%)	Uronic COOH (%)	Nonuronic COOH (%)	Uronic COOH / Total COOH (%)
8	10.90	8.95	1.95	82.1
6	12.08	9.4	2.68	77.8
7	12.53	11.09	1.44	88.5
9	14.80	11.65	3.15	78.7

Table 1 shows, however, that when the uronic COOH groups have been accounted for, there remain about 20% of the carboxyl groups that must occur in other positions in the glucose residues. The figures obtained have no absolute significance, but they reflect the fact that in oxycelluloses not all of the carboxyl groups are identical in their chemical properties. The value found for the nonuronic

carboxyl corresponds to 5-10 per 100 glucose residues. Such a number could be accommodated at the ends of macromolecular chains only if the degree of polymerization were very low – of the order of 20-10 – when the preparation would become brittle, lose its fibrous structure, and give solutions of negligible viscosity. The molecular weights of oxycelluloses prepared by the action of nitrogen dioxide cannot be measured by the existing methods. There is every reason to suppose, however, that these celluloses are of fairly high molecular weight. Cotton fibers, oxidized with nitrogen dioxide, lose part of their mechanical strength, but they differ little in appearance from unoxidized fibers; when dissolved in aqueous ammonia they give gels. According to our experiments, the viscosity of 0.5% solutions of the oxycelluloses in 0.2% caustic soda is at first high, but falls very rapidly (Figure 1).

All this indicates that the oxidized preparations have a fairly high degree of polymerization. In that case the number of nonuronic carbonyls found cannot be accomodated at the ends of chains, and it must be assumed that they are formed by the oxidation of secondary alcohol groups accompanied by scission of a C–C link in the pyran ring.

The work of Kenyon and coworkers [2] points to the reverse relation between total and uronic carboxyl groups, with the latter predominating. The cause of this is to be found in the fact that in the determination of COOH groups in Kenyon's experiments excessive lowering of the pH occurred owing to the presence of an inadequate amount of buffer; reaction was therefore not complete. Nevell [9] found values for the relative amounts of uronic and total COOH groups which were close to those found by us.

b) Aldehyde Groups in Celluloses Oxidized with Nitrogen Dioxide. Irrespective of the extent of oxidation, the content of aldehyde groups in preparations oxidized with nitrogen dioxide was very low (Table 2). Aldehyde groups were determined iodometrically. Oxidation with hypoiodite was carried out in a buffered medium having a pH of about 9 (0.1 M $Na_2B_4O_7$, 25°, 90 minutes). As we have shown [17], under these conditions α-hydroxy ketone groupings are not oxidized and therefore do not interfere in the determination.

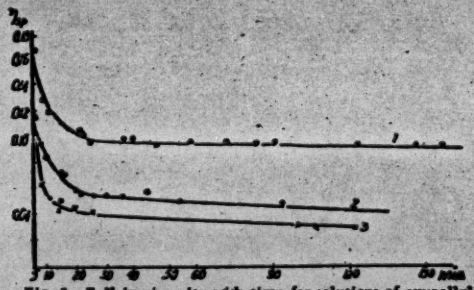


Fig. 1. Fall in viscosity with time for solutions of oxycelluloses in 0.2% NaOH (temperature 20 ± 0.05°; measurements taken every 4-5 minutes after beginning of dissolution): 1) for 0.5% solution of Preparation 6; 2) for 0.4% solution of Preparation 6; 3) for 0.4% solution of Preparation 2.

TABLE 2

Content of Aldehyde Groups in Celluloses Oxidized with Nitrogen Dioxide

Experiment No.	Oxidation conditions	COOH groups (%)	Aldehyde groups (%)	Number of aldehyde groups per 100 glucose residues
16	70 hours 21-25°	11.45	0.04	0.24
6	48 hours 20-22°	12.08	0.05	0.30
15	72 hours 20-23°	14.0	0.02	0.12
9	92 hours 15-20°	14.8	0.06	0.35
L1	96 hours 16-20°	17.2	0.04	0.24
L11	96 hours 16-20°	16.8	0.07	0.42

It is impossible to exclude the possibility that some of the aldehyde groups exist in these celluloses in the combined state; having entered into the formation of acetal or acylal groupings. Acylal groupings are very sensitive to alkali and will react with iodine under the conditions for the determination of aldehyde groups; they behave, in fact, like free aldehyde groups. Acetal groupings are more stable and may not be determinable by the iodometric method. However, in the oxycelluloses studied in the present investigation there is a negligible number of free aldehyde groups – which, if present, would bring about a reduction in the stability of the cellulose and would be oxidized by hypochlorite, hydrogen peroxide, and other oxidizing agents. It must be pointed out, when NO_2-oxidized celluloses are kept, the number of aldehyde groups present rises very rapidly, so that the values given in the table can be obtained only as freshly oxidized preparations.

c) Keto Groups in Celluloses Oxidized with Nitrogen Dioxide. It was very important to establish whether there were any keto groups in the oxycelluloses; the presence of such groups has been considered on several occasions, but there was an inadequate basis for the resolution of this question. The difficulty lies in the fact that only the hydroxylamine method of Meesook and Purves [11] has been used in the quantitative determination of carbonyl groups in oxycelluloses, and this is inapplicable to celluloses oxidized with nitrogen dioxide because these oxycelluloses contain appreciable numbers of lactone groupings, which react with hydroxylamine [18] under the conditions required in the determination of carbonyl; the results are therefore too high. Moreover, the carboxyl groups of these oxycelluloses cannot be neutralized before the carbonyl determination without the dissolution of an appreciable part of the preparation. We attempted to break the lactone linkages by bringing the preparations gradually to pH 8.5 (treatment with alkali) and then determining carbonyl groups, but even a very short time in the alkaline medium resulted in the formation of new aldehyde groups. Decyclization of lactones by a one-hour treatment in hot 1% hydrochloric acid did not give better results: again there was some hydrolysis and the number of aldehyde groups increased. We therefore decided to apply the alcohol variant of the hydroxylamine method to the estimation of carbonyl groups in these oxycelluloses. In this method, which was developed by us [19], the determination is carried out at pH 4 with a solution of hydroxylamine hydrochloride in 90% alcohol: at this pH the lactone groupings do not take part in the reaction. As the acidity of the oxycelluloses was very high and it could not be suppressed completely by the use of an alcohol medium at pH 4, a correction was made in the titration results for the residual acidity of the oxycellulose. For this purpose, a separate, weighed sample of the oxycellulose was introduced into 90% alcohol and titrated in absence of hydroxylamine to pH 3.2 with 0.1 N NaOH.

The correctness of the carbonyl content, so determined, was checked by determining the nitrogen content of the oxycellylose oxime, prepared, as indicated, in an acid alcoholic medium and then washed with alcohol. The nitrogen content, after subtraction of the component attributable to nitric ester groups, was 91-95% of the value calculated from the carbonyl content found by titration (Table 3).

TABLE 3

Verification of the Method of Determining Carbonyl Groups by Comparison with Nitrogen Determinations on Preparations Condensed with Hydroxylamine Hydrochloride

Experiment No.	N content before condensation with $NH_2OH \cdot HCl$ (%)	N content after condensation with $NH_2OH \cdot HCl$ (%)	Increase in N content due to condensation (mg-equiv. per 100 g)	Carbonyl content found by titration (mg-equiv. per 100 g)	$\frac{N}{CO}$ (%)
30	0.16	1.51	96	105	91.8
32	0.18	1.75	112	123	91.0
1-c	0.18	1.75	112	117	95.7

The oxidized glucose residues contain single keto groups and also, probably, diketone groupings. The presence of α-hydroxy ketone groupings was confirmed by the endiol reaction with a phosphoric-arsenic-tungstic reagent (Benedict's), which we have developed for celluloses [17]. In this reaction, all of the celluloses oxidized with nitrogen dioxide gave a dark-blue coloration, which indicates high contents of hydroxy ketone groupings. Tentative quantitative determinations of hydroxy ketone groupings with the aid of this reaction gave much higher values for NO_2-oxidized celluloses than for oxycelluloses of other types.

Table 4 gives the total carbonyl content and the contents of aldehyde, ketone, and hydroxy ketone groupings in oxycelluloses obtained by oxidation with oxides of nitrogen.

TABLE 4

Contents of Carbonyl Groups in NO_2-oxidized Celluloses

Preparation No.	COOH (%)	Total carbonyl groups (%)	Aldehyde groups (%)	Ketone groups (%)	α-Hydroxy ketone groupings (%)
28	1.93	0.54	0.43*	0.11	0.095
33-L	7.5	1.02	0.02	1.00	—
34-L	9.9	3.04	0.01	3.03	—
30	11.8	2.94	0.26*	2.72	0.62
1-c	17.20	3.28	0.04	3.24	—
32	17.21	3.40	0.35*	3.05	0.53

* The preparations were kept for nine months.

TABLE 5

Content of α-Hydroxy Ketone Groupings at various Stages of the Oxidation of Cellulose

Preparation No.	Number of groupings per 100 glucose residues			Hydroxy ketone / Total ketone (%)	Mol. wt. of structural unit
	COOH	Total ketone	Hydroxy ketone		
28	7.0	0.64	0.55	86	163.1
30	44.3	16.36	3.74	23	168.6
19	53.9	18.80	3.65	19	170.0
32	65.8	18.72	3.56	24	172.0

For the determination of α-hydroxy ketone groupings, a 0.1-g or 0.05-g sample of oxycellulose was covered with 1 ml of 10% sodium carbonate in a large test tube and heated in a water bath at 80° for 20 minutes. The mixture was cooled, 0.5 ml of Benedict's reagent was added, and, after 15 minutes, the volume was made up to 30 ml with water. The solution was passed through a glass filter, and the intensity of the color was measured on a photometer with an M-57 yellow-green filter (574 mμ). The content of hydroxy ketone groupings was calculated from a calibration curve obtained for ascorbic acid, the reaction being carried out under the same conditions, but without the treatment with hot sodium carbonate solution. On a percentage basis, at the beginning of the oxidation α-hydroxy ketone groupings predominated, whereas in the later stages other, probably diketone groupings, predominated (Table 5).

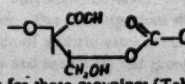
d) Carbonic Ester Groupings. Glucose residues in the cellulose chain that have been oxidized with opening of the ring and formation of carbonic ester groupings  should be particularly sensitive to the action of an alkaline medium. Analyses for these groupings (Table 6) by the method that we have developed [16] showed that in nitrogen dioxide oxidation practically no such groupings are formed, for the preparations do not yield carbon dioxide when treated with 1% caustic soda in the cold.

TABLE 6

Elimination of Carbon Dioxide from Oxycelluloses in Treatment with Alkali

Preparation No.	COOH groups (%)	CO_2 eliminated (% on weight of sample)	CO_2 eliminated (molecules per 100 glucose residues)
Unoxidized cellulose	0.04	0.017	0.067
27	2.50	0.018	0.071
22	6.35	0.077	0.30
26	13.30	0.081	0.32

TABLE 7

Forms of Nitrogen in Celluloses Oxidized with Nitrogen Dioxide

Preparation No.	COOH groups (%)	Nitrogen		
		Total (%)	as nitric ester (%)	Difference
28	12.93	0.72	0.71	0
27	2.53	1.26	1.03	+ 0.23
22	6.35	2.54	2.33	+ 0.21
26	13.3	0.21	0.11	+ 0.10

The traces of carbon dioxide obtained from strongly oxidized preparations were probably formed by the decarboxylation of rather unstable oxidation products, and they cannot be regarded as proof of the presence of carbonic esters.

e) Form in which Nitrogen Occurs in Celluloses Oxidized with Nitrogen Dioxide. After being oxidized with nitrogen dioxide, celluloses always contain some nitrogen, the amount of which varies greatly according to the oxidation conditions. In the course of the oxidation, the nitrogen content rises at first, and then, after some time, begins to fall, as indicated in Fig. 2. The total nitrogen was determined by the Kjeldahl method, the preparation being first reduced with zinc and salicylic acid. Also, nitric ester nitrogen was determined by the Schultz-Tiemann method [20] (reduction with ferrous chloride and volumetric determination of the nitric oxide evolved). The two methods gave closely agreeing results, which indicates that all of the nitrogen present in these oxycelluloses is in the form of ester groupings (Table 7).

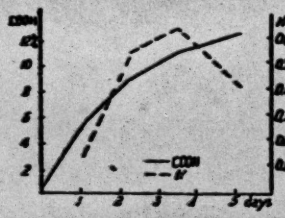


Fig. 2. Variation of nitrogen and carboxyl contents of cellulose with extent of oxidation.

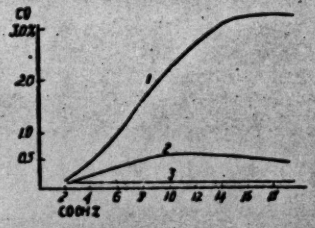


Fig. 3. Carbonyl content as a function of the extent of oxidation of cellulose: 1) keto groups; 2) α-hydroxy ketone groupings; 3) aldehyde groups.

Discussion of Experimental Results

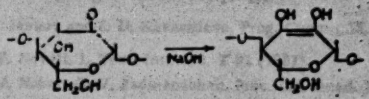
According to the oxidation mechanism proposed by Kenyon and coworkers, the oxidation of cellulose with nitrogen dioxide begins with the esterification of primary OH groups by the traces of nitric acid present. The second stage of the reaction consists in the oxidative denitration of the nitric ester groupings by the action of N_2O_4 in presence of HNO_3. The presence of nitrogen in the oxycelluloses is explained by these authors by the esterification of a few secondary hydroxyls, with the formation of ester groupings that are not subsequently hydrolyzed. Our experiments on the oxidation of cellulose, and also of simple hydroxy compounds [21], are in accord with the intermediate formation of nitric ester groupings in the oxidation. This view, however, must be extended, since not only primary, but also secondary OH groups take part in the reaction. Our investigations show that, in the reaction between nitrogen dioxide and isopropyl alcohol, intermediate formation of a nitric ester occurs; hydrolysis of this yields acetone. Analogous reactions were established for the primary and secondary OH groups in various compounds (ethylene glycol, 1,2-propanediol, methyl glucoside).

The formation of keto groups in oxycelluloses proves that in polysaccharides OH groups can react by this mechanism, i.e. after the formation of a nitric ester, under certain conditions the ester grouping may be eliminated with simultaneous oxidation.

Our work has shown that the oxidation of cellulose with nitrogen dioxide is not specific, for it brings about oxidative changes in different directions. These changes, however, are sufficiently characteristic to give us grounds for placing this oxidizing agent in a special group. Both primary and secondary alcohol groups are oxidized with formation, respectively, of carboxyl groups at C-6 and keton groups at C-2 or C-3. The oxidation of primary alcohol groups proceeds to a very much greater extent than that of secondary alcohol groups, which is in accord with the idea of the formation of nitric esters in the first stage of the reaction. Further oxidation occurs at the keto groups with opening of the ring, but the extent to which this occurs is only slight. Aldehyde groups are essentially absent, and the aldehyde content can be neglected. The content of keto groups rises as the carboxyl content rises, and it may attain more than 18 per 100 glucose residues (Fig. 3).

Judging from the strong endiol reaction, a considerable proportion of the keto groups are present in the form of α-hydroxy ketones, the amount of which corresponds closely to the total keto group content at the beginning of the

reaction, but falls, when expressed as a percentage of the total number of keto groups, as the reaction proceeds.



Some authors have remarked on the great similarity in properties between the oxycelluloses obtained by nitrogen dioxide oxidation and those obtained by periodic acid oxidation – there is the instability of both types of oxycelluloses in an alkaline medium [10], the formation of new carboxyl groups when the preparation stands in an alkaline medium, the insolubility of the nitric esters [22], etc. – and they have tended to explain this resemblance by the presence of dialdehyde groupings in NO_2-treated cellulose. Direct determination shows that there are very few aldehyde groups in these oxycelluloses. Moreover, the hydroxy ketone groupings, which are present in large numbers, are very similar to dialdehyde groupings in their effect on the properties of the oxycelluloses: they also bring about a great reduction in stability to alkali, being converted by alkali into endiols, and then further into carboxyl groups by oxidative scission of the ring. There is therefore no need to postulate the presence of dialdehyde groupings in oxycelluloses obtained by nitrogen dioxide oxidation. Also, the formation of these groups is difficult to reconcile with the proposed oxidation mechanism through the intermediate stage of nitric esters and also with the great ease with which aldehyde groups are oxidized by nitrogen dioxide.

On the other hand, it is quite probable that, when there are high contents of both carboxyl and keto groups in cellulose preparations obtained by nitrogen dioxide oxidation, glucose residues occur which contain both of these groups simultaneously. This accumulation of functional groups in one structual unit must result in a further reduction in the stability of such units and in the ready breakdown of the macromolecule. The probability of the presence of such highly oxidized units has been recently confirmed by the isolation of 3,5-dihydroxy-4H-pyran-4-one from the hydrolyzate of an oxycellulose [23].

SUMMARY

1. The oxidation of cellulose by nitrogen dioxide does not consist in the specific oxidation of primary alcohol groups, this reaction being always accompanied by the oxidation of secondary alcohol groups.

2. In celluloses oxidized with nitrogen dioxide, most of the carboxyl groups formed are in the 6-positions of the glucose residues. Some of the carboxyl groups are formed as a result of oxidative scission of the pyran ring.

3. Celluloses oxidized with nitrogen dioxide contain many carbonyl groups (as many as 19 groups per 100 glucose residues, the number of carboxyl groups then being 65). In freshly oxidized preparations most of the carbonyls are keto groups, and the content of aldehyde groups is low (not more than 0.3 per 100 glucose residues).

4. Celluloses oxidized with nitrogen dioxide do not contain peroxy and carbonic ester groupings. All of the nitrogen in these oxycelluloses is present in the form of nitric ester groupings.

5. The experimental material obtained supports the suggestion that oxidation proceeds with intermediate formation of nitric esters. It is necessary to assume that ester formation and the oxidative hydrolysis of the product can occur not only at primary OH groups, but also at secondary OH groups in the glucose residues of the cellulose macromolecule.

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FORMATION OF LOW-MOLECULAR-WEIGHT POLYMERS OF VINYL ETHERS IN PRESENCE OF BENZOYL PEROXIDE

M. F. Shostakovsky, E. S. Shapiro, and F. P. Sidelkovskaya

As is well known, benzoyl peroxide is very extensively used as an initiator of the polymerization of unsaturated compounds. Many investigations have been carried out on the decomposition of benzoyl peroxide in various media. One of us and coworkers [1] studied the reaction of butyl and phenyl vinyl ethers with substantial amounts of benzoyl peroxide (10-50% by weight), and it was shown that, under the conditions employed, benzoyl peroxide mainly plays the part of an adding agent reacting at the double bond of the vinyl ether. The clear viscous products obtained in this reaction had an acylal structure $C_6H_5COOCH_2CH\langle^{OR}_{OCOC_6H_5}$. It was found also that reduction in the amount of peroxide taken for reaction resulted in the formation of products having higher molecular weights than that of the addition product.

It was considered to be of interest to study the interaction between vinyl ethers and catalytic amounts of benzoyl peroxide. It was important to establish whether a polymerization reaction occurred under these conditions, for it has been shown quite recently that it is possible in principal to bring about the polymerization of vinyl ethers under the influence of other free-radical initiators [2-4].

In the present investigation we used isopropyl and butyl vinyl ethers at two different temperatures. The experiments were carried out in sealed tubes for different periods of time, the benzoyl peroxide concentrations being 10, 5, 2.5, and 1% by weight for the first ether and 1, 0.5, 0.2, and 0.1% by weight for the second. It was shown that some undecomposed benzoyl peroxide still remained after five hours when butyl vinyl ether was heated with 1% of benzoyl peroxide at 60°; after ten hours the whole of the peroxide had decomposed and the yield of viscous reaction product had increased appreciably. Experiments were carried out in which the tubes were sealed off a) in the atmosphere and b) at a residual pressure of 1-2 mm. However, no difference was found in yield of product or in rate of decomposition of benzoyl peroxide, and in subsequent experiments the tubes were always sealed off in the air. A period of heating of 120-140 hours was found to be sufficient for the obtaining of reproducible results in different parallel experiments, both with respect to total yield and with respect to the constants of the polymeric product. Control experiments showed that no thermal polymerization of the vinyl ether was to be observed under these conditions of prolonged heating.

Interaction between butyl vinyl ether and benzoyl peroxide under the above-described conditions resulted in the formation of colorless polymeric products in very low yield (1-5% on the amount of the ether taken for reaction). These products are completely stable to storage: they do not eliminate benzoic acid, as the acylal addition products do. In this respect they differ greatly from the products obtained by heating isopropyl vinyl ether with 5-10% of benzoyl peroxide: these also gradually eliminate benzoic acid. The polymeric products are soluble in all organic solvents, but most readily in ether.

The results of experiments carried out at 60° and 80° are given in Tables, 1, 2, and 3, from which it will be seen that, under the given conditions, the following regular behavior is observed: with reduction in the benzoyl peroxide concentration the yield (on the amount of peroxide taken) and molecular weight of the polymeric product increase and its refractive index and density diminish. The temperature dependence of the reaction must be emphasized. At a given benzoyl peroxide concentration (0.5, 0.2, or 0.1%) the yield and molecular weight of the polymeric product are considerably higher at 80°. The change in the constants of the polymeric products is still more marked, and the products become closer in elementary analysis to poly[butyl vinyl ether] (Table 4). On the other hand, the constants and analytical results for the products obtained with 10% and 5% of benzoyl peroxide differ greatly from those for poly[isopropyl vinyl ether] (Tables 3 and 5). This is in complete accord with the fact that these products are closer to acylals in their properties.

Hence, interaction between an alkyl vinyl ether and benzoyl peroxide taken in a concentration of less than 1% results in the polymerization of the ether to polymers of low molecular weight. The process can probably be

TABLE 1

Reaction of Butyl Vinyl Ether with Benzoyl Peroxide at 60°

Experiment No.	Amount taken		Duration of heating (hours)	Yield of reaction products (% on benzoyl peroxide)	Constants		
	Butyl vinyl ether (g)	Benzoyl peroxide (% by weight)			n_D^{20}	d_4^{20}	M
3	315.5	1	120	327	1.4852	1.0062	473.9; 476
10	260	1	120	328.8	1.4858	1.0036	561.6; 550.5
7	160	0.5	120	425	1.4790	0.9866	649.6; 694
25	160	0.5	140	436	1.4740	—	654.1; 683.7
26	300	0.2	140	671.6	1.4714	0.9717	961.4; 876.2
24	200	0.2	140	635	1.4720	—	—

TABLE 2

Reaction of Butyl Vinyl Ether with Benzoyl Peroxide at 80°

Experiment No.	Amount taken		Duration of heating (hours)	Yield of reaction products (% on benzoyl peroxide)	Constants		
	Butyl vinyl ether (g)	Benzoyl peroxide (% by weight)			n_D^{20}	d_4^{20}	M
15	208	1	120	482.3	1.4732	—	—
20	150	1	141	546.6	1.4720	0.9681	631.1; 684.4
8	350	0.5	120	787.4	1.4680	0.9611	902.7; 950.3
18	250	0.5	144	727.5	1.4665	0.9611	978.5; 947.3
22	130	0.5	140	721.5	1.4670	—	—
9	600	0.2	120	1180	1.4635	0.9490	1215; 1185
14	302	0.2	120	1406	1.4640	—	—
12	452	0.1	120	2062	1.4619	—	—
21	200	0.1	140	2175	1.4590	—	1100; 1036

TABLE 3

Heating of Isopropyl Vinyl Ether with Benzoyl Peroxide at 60° for 120 hours

Experiment No.	Amount taken		Yield of reaction products (% on benzoyl peroxide)	Constants		
	Isopropyl vinyl ether (g)	Benzoyl peroxide (% by weight)		n_D^{20}	d_4^{20}	M
1	5	10	194	1.5002	1.070	331.5; 331.3
2	10	5	228	1.4915	1.053	400
12	20	2.5	344	1.4892	1.044	—
3	50	1	340	1.4790	1.021	561.6; 516.2

represented as follows: the benzoate radicals formed by the decomposition of benzoyl peroxide react at the double bond of the alkyl vinyl ether and initiate polymerization, but the resulting chain reaction is slow and gives short polymer chains $C_6H_5COO-(CH_2-\underset{\underset{OR}{|}}{CH})_n\ldots$ In this connection it is of interest to compare the results for the polymerization of some vinyl ethers in presence of another radical initiator, e.g. 2,2'-azobis[2-methylpropionitrile].

For butyl vinyl ether in presence of the azo nitrile, the yield of polymer ranges from 9% to 25% (on the amount of the ether taken), depending on the amount of initiator used. Similar yields of polymer are obtained from isopropyl and cyclohexyl vinyl ethers in presence of the azo nitrile [4]. Phenyl vinyl ether does not polymerize so readily in presence of the same initiator [3], the yields of polymeric products of molecular weight 700–800 being 7–14% on the amount of the ether taken.

TABLE 4

Results of Elementary Analysis for Polymers Obtained in Experiments with Butyl Vinyl Ether

Experiment No.	Benzoyl peroxide concentration (% by weight)	Experimental temperature in °C (duration in hours)	Analysis		Experiment No.	Benzoyl peroxide concentration (% by weight)	Experimental temperature in °C (duration in hours)	Analysis	
			C (in %)	H (in %)				C (in %)	H (in %)
5	1	60 (10)	70.34	8.79	20	1	80 (140)	71.41	10.39
			70.14	8.81				71.26	10.43
3	1	60 (120)	70.78	9.68	8	0.5	80 (120)	71.25	11.04
			70.68	9.80				71.04	10.97
7	0.5	60 (120)	70.93	10.13	9	0.2	80 (120)	70.86	11.28
			71.16	10.20				70.84	11.36
26	0.2	60 (140)	70.70	10.68	12	0.1	80 (120)	71.28	11.60
			70.85	10.73				71.47	11.66

Note: Theoretical elementary composition for $CH_2=CHOC_4H_9$, C 71.92%, H 12.08%. Theoretical elementary composition for $C_6H_5COOCH_2CH(OC_4H_9)(OCOC_6H_5)$: C 70.15%, H 6.48%.

TABLE 5

Results of Elementary Analysis for Reaction Products Obtained in Experiments with Isopropyl Vinyl Ether

Experiment No.	Benzoyl peroxide concentration (% by weight)	Experimental temperature in °C (duration in hours)	Analysis		Experiment No.	Benzoyl peroxide concentration (% by weight)	Experimental temperature in °C (duration in hours)	Analysis	
			C (in %)	H (in %)				C (in %)	H (in %)
1	10	60 (130)	69.05	7.81	12	2.5	60 (130)	69.36	8.40
			68.87	7.82				69.36	8.47
2	5	60 (130)	68.61	8.27	3	1	60 (130)	69.78	9.27
			68.76	8.14				69.44	9.39

Note: Theoretical elementary composition for $CH_2=CHOC_3H_7$-i, C 69.79%, H 11.69%. Theoretical elementary composition for $C_6H_5COOCH_2CH(OC_3H_7\text{-}i)(OCOC_6H_5)$: C 69.52%, H 6.14%.

TABLE 6

Heating of Butyl Vinyl Ether with Benzoyl Peroxide at 60°

Experiment No.	Amount taken		Method of sealing tube	Duration of heating (hours)	Peroxide remaining undecomposed (%)	Yield of reaction product (%)	Constants		
	Butyl vinyl ether	Benzoyl peroxide (% by weight)					n_D^{20}	d_4^{20}	M
1	49.4	0.5	In the air	5	8.4	1	1.5049	—	—
2	49.8	0.5	In a vacuum	5	9.7	1	1.5040	—	—
5	75	0.75	In the air	10	None	1.93	1.4946	1.0312	399.4; 409.1
6	90	0.5	In the air	10	None	1.22	1.4880	Not determined	537.7; 523

It follows from this comparison that, in polymerizing in presence of free-radical initiators, vinyl ethers give polymers of comparatively low molecular weight in low yield.

In our case, the part played by benzoyl peroxide in the polymerization of vinyl ethers is even more limited, mainly owing to the fact that at the peroxide concentrations of more than 2% the action of the benzoyl peroxide as an adding agent – reacting at the double bond of the vinyl ether – begins to become effective. This action results in the inhibition of the polymerization reaction.

EXPERIMENTAL

Procedure. Weighed amounts of alkyl vinyl ether and benzoyl peroxide were introduced into a glass tube. When low concentrations were used (of the order of 0.1 or 0.2%), the solutions were prepared separately and then poured into the tubes. The tubes were sealed off either in the air or in a vacuum (residual pressure 1-2 mm). The tubes were placed in a thermostat at 60° or 80°, and were kept there for the required time. The tubes were then cooled, and their contents were transferred to a distillation apparatus. The alkyl vinyl ether was distilled off at 5 mm at room temperature in a current of nitrogen, and it was collected in a coiled receiver cooled to a temperature of −70 to −75°. The polymeric residue was brought to constant weight by exposing it to a vacuum (2-3 mm) at 60° (generally for 15-18 hours). The results of all of the experiments are given in Tables 1, 2, and 3. The results of some experiments that were not carried out under standard conditions are given in Table 6.

Control Experiments. a) At 60°. A tube containing 90.1 g of butyl vinyl ether was sealed in the air. After being heated under the above-described conditions for 120 hours, the contents were distilled and gave 89 g of butyl vinyl ether. The residue amounted to 0.08 g, or 0.09% on the weight of the ether taken for reaction.

b) At 80°. Butyl vinyl ether (90 g) was heated in a sealed tube for 140 hours. After the usual treatment of the contents, the residue amounted to 0.1 g, or 0.11% on the weight of the ether taken for reaction. Hence, under the given conditions practically no thermal polymerization occurs.

SUMMARY

1. The interaction of butyl and isopropyl vinyl ethers with benzoyl peroxide was studied at peroxide concentrations of 0.1-10%.

2. It was shown that, at benzoyl peroxide concentrations of 2% and less, the vinyl ether polymerizes with formation of products of low molecular weight. At peroxide concentrations of 5% and 10%, addition and polymerization reactions occur simultaneously.

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BRIEF COMMUNICATIONS

PREPARATION OF HEXAALKOXYDITITANOXANES $(RO)_3Ti-O-Ti(OR)_3$

A. N. Nesmeyanov, O. V. Nogina, and R. Kh. Freidlina

In a previous paper [1] we described the preparation of trialkoxytitaniums, and we also described briefly the reaction occurring when tripropoxy- and tributoxy-titaniums are oxidized by air. Compounds of composition $(C_3H_7O)_2TiO$ and $(C_4H_9O)_2TiO$ were isolated from the reaction mixture. These dialkoxytitanium oxides are solids that are readily soluble in all inert organic solvents. We did not succeed in crystallizing them. A more detailed study of the oxidation of trialkoxytitaniums has shown that, depending on the reaction conditions, not only dialkoxytitanium oxides, but also hexaalkoxydititanoxanes are formed.

When triethoxytitanium was oxidized, the main product was hexaethoxydititanoxane. By repeated recrystallization of the mixture of solid reaction products, hexaethoxydititanoxane was finally isolated in the pure state. This compound has not been described in the literature.

As two authors of this paper have shown in collaboration with r ainina [2], hexaethoxydititanoxane cannot be prepared by the hydrolysis of tetraethyl orthotitanate; when tetraethyl orthotitanate reacts with water at a molar ratio of 2:1, the product is not hexaethoxydititanoxane, formed in accordance with the equation

$$2(C_2H_5O)_4Ti + H_2O \rightarrow (C_2H_5O)_6Ti_2O + 2C_2H_5OH,$$

but octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$.

Bradley, Gaze, and Wardlaw [3] have recently reported that in the reaction between tetraethyl orthotitanate and water at a molar ratio of 2:1 they obtained not hexaethoxydititanoxane, but a substance containing 66.3-67.8% of ethoxyl groups and 25.7-26.1% of titanium. The authors did not succeed in establishing the structure of this compound. It is clear that they obtained the octaethoxytrititanoxane already described [2] (calculated ethoxyl content 67.1%, titanium content 26.81%).

Until now, there has been no method available for the synthesis of hexaalkoxydititanoxanes. There are reports of the formation of hexabutoxydititanoxane [4] and hexaallyloxydititanoxane [5] in the thermal decomposition of the corresponding tetraalkyl orthotitanates. In these investigations, however, the reaction products were analyzed without a preliminary purification, and then only for titanium content; the values found differed greatly from the calculated values. There is also a report that hexabutoxydititanoxane was obtained in the hydrolysis of tetrabutyl orthotitanate [6], but again the analysis, which was only for titanium, was carried out on the unpurified product. It should be noted that in all of these cases hexaalkoxydititanoxanes were described as viscous liquids or semisolids. The hexaethoxydititanoxane that we have prepared by the oxidation of triethoxytitanium was obtained as a white crystalline substance after crystallization from a mixture of alcohol and petroleum ether; it was readily soluble in alcohol and benzene, but less readily soluble in petroleum ether.

Hexapropoxy- and hexabutoxy-dititanoxanes were prepared by the transesterification of hexaethoxydititanoxane with propyl and butyl alcohols. We succeeded in crystallizing these substances from a mixture of the corresponding alcohol and petroleum ether. The hexaalkoxydititanoxanes obtained were exceptionally hygroscopic and were very readily hydrolyzed. Cryoscopic determination of the molecular weight of hexaethoxydititanoxane in benzene showed that the substance associates in solution, and only at high dilution did the molecular weight found approximate to that calculated for the nonassociated compound.

EXPERIMENTAL

Preparation of Hexaethoxydititanoxane $(C_2H_5O)_6Ti_2O$

a) Preparation of Triethoxytitanium $(C_2H_5O)_3Ti$. Potassium (8 g) was introduced into a three-necked flask filled with nitrogen and fitted with reflux condenser and mercury-sealed stirrer. A solution of 24 g of tetraethyl

orthotitanate in 200 ml of absolute ethanol was then poured into the flask, and there was an immediate dark-brown coloration. When the whole of the potassium had reacted, the reaction mixture was transferred, by the aid of nitrogen under pressure, to a funnel with a No. 3 glass filter. The air contained in the cylindrical funnel was first carefully displaced by dry nitrogen. The precipitate was filtered off under suction and washed three or four times with absolute ethanol to remove potassium ethoxide and then twice with petroleum ether at 30-50°. The reaction product was then dried under reduced pressure (2-3 mm) in a current of dry nitrogen at room temperature for 10-15 minutes. The product so obtained can be used for the oxidation. The carefully dried substance (dried for about one hour under the conditions indicated) is of a reddish-lilac color. It is sparingly soluble in the usual organic solvents, and it is extremely sensitive to oxygen and to atmospheric moisture. In its properties it is very close to the previously described [1] tripropoxy- and tributoxy-titanium.

b) Preparation of Hexaethoxydititanoxane. The dry triethoxytitanium prepared as described above was oxidized directly on the funnel by means of a current of dry oxygen. The oxidation products gradually flowed into the receiver in the form of a viscous liquid. The oxidation of the triethoxytitanium obtained by the reduction of 24 g of tetraethyl orthotitanate was complete in 2.5-3 hours. The liquid reaction products were evaporated at 30-40° under reduced pressure (25-40 mm). The residue was recrystallized three times from a 1:1 mixture of ethanol and petroleum ether (50-70°). The yield was 2 g; m.p. 132-134°.

	Found %:	C 37.81; 37.70;	H 7.68; 7.87;	Ti 25.02; 25.11
$C_{12}H_{30}O_7Ti_2$.	Calculated %:	C 37.71;	H 7.91;	Ti 25.07

Found: M* 397.7
Calculated: M 381.8

Preparation of Hexapropoxydititanoxane ($(C_3H_7O)_6Ti_2O$)

Hexaethoxydititanoxane (0.9 g) was dissolved by warming it with 2 ml of propyl alcohol, and the solution was heated under conditions that permitted the removal of alcohols by distillation, the bath temperature being raised very slowly. At a vapor temperature of 77-80°, 0.67 g of liquid – mainly ethanol – came over (calculated amount 0.65 g). A further 2 ml of propyl alcohol was then added, and the distillation operation was repeated. The residue remaining after the distillation of the excess of propyl alcohol was recrystallized from a 1:1 mixture of propyl alcohol and petroleum ether.

	Found %:	C 46.52; 46.61;	H 9.08; 9.2½;	Ti 20.16; 20.41
$C_{18}H_{42}O_7Ti_2$.	Calculated %:	C 46.36;	H 9.08;	Ti 20.54

Preparation of Hexabutoxydititanoxane ($(C_4H_9O)_6Ti_2O$)

Hexaethoxydititanoxane (1.1 g) was dissolved by heating it with 5 ml of butyl alcohol. The mixture of alcohols was distilled off at 35 mm from a bath at 50-55°. The reaction mixture was then cooled, and a further 5 ml of butyl alcohol was added. The mixture of alcohols was distilled off at 35 mm from a bath at 65-70°. The last operation was repeated. The residue remaining in the flask after the distillation of the excess of butyl alcohol the last traces of which were removed under reduced pressure (2 mm) at 50-60°, was analyzed.

	Found %:	C 52.67; 52.43;	H 9.83; 9.80;	Ti 16.89; 16.88
$C_{24}H_{54}O_7Ti_2$.	Calculated %:	C 52.36;	H 9.88;	Ti 17.40

In another experiment the transesterification treatment was applied to some hexaethoxydititanoxane which analysis showed to be of inadequate purity, and the hexabutoxydititanoxane obtained was purified by two recrystallizations from a 3:1 mixture of petroleum ether and butyl alcohol.

	Found %:	C 52.32; 52.36;	H 9.74; 9.73;	Ti 17.22; 17.27
$C_{24}H_{54}O_7Ti_2$.	Calculated %:	C 52.36;	H 9.89;	Ti 17.40

Hexabutoxydititanoxane is readily soluble in alcohols and benzene, but not so readily soluble in petroleum ether.

SUMMARY

1. Hexaethoxydititanoxane was prepared by the oxidation of triethoxytitanium.

* The value of the molecular weight obtained for these substances varied from one determination to another. Thus, for another sample, of about the same weight, the molecular weight was found to be 500.

2. Hexapropoxy- and hexabutoxy-dititanoxanes were prepared by the transesterification of hexaethoxy-dititanoxane.

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ORGANOBORON COMPOUNDS

COMMUNICATION 6. ACTION OF PHOSPHORUS PENTACHLORIDE ON DIARYLBORINIC ESTERS. SYNTHESIS OF DIARYLCHLOROBORINES

B. M. Mikhailov and N. S. Fedotov

We have found that phosphorus pentachloride reacts with propyl diphenylborinate with formation of chlorodiphenylborine (diphenylborinic chloride) in high yield, together with propyl chloride and phosphoryl chloride in accordance with the equation:

$$(C_6H_5)_2BOC_3H_7 + PCl_5 = (C_6H_5)_2BCl + POCl_3 + C_3H_7Cl.$$

Phosphorus pentachloride reacts similarly with isobutyl di-1-naphthylborinate with formation of chlorodi-1-naphthylborine in 70% yield.

Diarylborinic chlorides have previously not been readily accessible owing to the absence of a convenient method of preparation. The only organoboron compound of this type that has been prepared — chlorodiphenylborine — was obtained in low yield by heating diphenylmercury with dichlorophenylborine at 320° for one day [1].

The method that we have found makes diarylborinic chlorides accessible and opens up wide possibilities for their use in synthesis.

EXPERIMENTAL

Chlorodiphenylborine. Phosphorus pentachloride (18.6 g) was added with shaking to 20 g of propyl diphenylborinate [2] b.p. 142-143° (5 mm) contained in a flask fitted with a Vigreux column. Reaction occurred with evolution of heat. When reaction was complete, propyl chloride and phosphoryl chloride were removed under reduced pressure (the coiled receiver being cooled with solid carbon dioxide), and the chlorodiphenylborine was then distilled off, the yield being 12.4 g (70%): b.p. 119-120° (3 mm); d_4^{20} 1.1037.

Found %: B 5.50; C 72.15; H 5.01

$C_{12}H_{10}BCl$. Calculated %: B 5.40; C 71.89; H 4.99

By fractional distillation 5 g of propyl chloride and 12.9 g of phosphoryl chloride were isolated.

Chlorodi-1-naphthylborine. Isobutyl di-1-naphthylborinate (m. p. 102-104°) was prepared by the action of 1-naphthylmagnesium bromide on triisobutyl borate, and a portion (20 g) was warmed with benzene (20 ml) until dissolved. Phosphorus pentachloride (12.3 g) was added to the resulting solution in portions, and when reaction was complete isobutyl chloride and phosphoryl chloride were driven off at the water pump. Fractionation of the residue from a pear-shaped flask gave 12.6 g (70%) of chlorodi-1-naphthylborine, b.p. 213-215° (1.5 mm), in the form of a viscous oil.

Found %: B 3.50, Cl 11.45

$C_{20}H_{14}BCl$. Calculated %: B 3.60; Cl 11.82

SUMMARY

Diarylchloroborines were prepared by the action of phosphorus pentachloride on diarylborinic esters.

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ORGANOBORON COMPOUNDS

COMMUNICATION 7. ACTION OF PHOSPHORUS PENTACHLORIDE ON ARENEBORONIC ESTERS. SYNTHESIS OF ARENECHLOROBORONIC ESTERS

B. M. Mikhailov and T. V. Kostroma

When an areneboronic ester is mixed with one equivalent of phosphorus pentachloride, reaction occurs with formation of an arenechloroboronic ester (an alkoxyarylchloroborine), an alkyl chloride, and phosphoryl chloride in accordance with the equation:

$$ArB(OR)_2 + PCl_5 = ArB\begin{matrix}Cl\\OR\end{matrix} + RCl + POCl_3$$

Ar = C_6H_5, o-$CH_3C_6H_4$.

By this method we prepared butyl benzenechloroboronate and isobutyl o-toluenechloroboronate from dibutyl benzeneboronate and diisobutyl o-tolueneboronate, respectively, these being the first representatives of a new type of boron compounds, in which boron is attached to an organic radical, halogen, and an alkoxy group.

EXPERIMENTAL

Butyl Benzenechloroboronate

Phosphorus pentachloride (41.7 g) was added in portions with constant vigorous agitation to 44.8 g (0.2 mole) of dibutyl benzeneboronate, contained in a Claisen flask. When the exothermic reaction was complete, butyl chloride and phosphoryl chloride were removed under reduced pressure (they were trapped in a coiled receiver cooled with solid carbon dioxide), and fractionation of the residue gave 29.5 g (75%) of butyl benzenechloroboronate, obtained as a colorless liquid b.p. 104-105° (9 mm) and d_4^{20} 0.9962.

Found %: B 5.61; Cl 18.3

$C_{10}H_{14}BOCl$. Calculated %: B 5.59; Cl 18.07

In addition, 17.4 g of butyl chloride and 27.4 g of phosphoryl chloride were obtained.

Isobutyl o-Toluenechloroboronate

Reaction was between 24.8 g (0.1 mole) of diisobutyl o-tolueneboronate and 20.8 g of phosphorus pentachloride. The procedure was as before.

Distillation gave 18.1 g (86%) of isobutyl o-toluenechloroboronate, b.p. 114-115° (10 mm), 110-111° (8 mm), in the form of a colorless liquid which fumed in air; d_4^{21} 0.9918.

Found %: B 5.40; Cl 16.3

$C_{11}H_{16}BOCl$. Calculated %: B 5.22; Cl 16.8

In addition, 8 g of isobutyl chloride and 11.7 g of phosphoryl chloride were obtained.

SUMMARY

When benzeneboronic and o-tolueneboronic esters were treated with phosphorus pentachloride, benzenechloroboronic and o-toluenechloroboronic esters were obtained, these being the first representatives of a new type of boron compounds.

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REACTIONS OF HYDROGEN FLUORIDE WITH DIAZO KETONES

I. L. Knunyants, Ya. M. Kisel, and E. G. Bykhovskaya

In 1915 Nierenstein and coworkers made a detailed investigation of the reaction of diazomethane with carboxylic acid chlorides [1] and found that the main product was the corresponding halo ketone.

Later, in a study of this reaction, Arndt and coworkers [2], and shortly afterwards Robinson and Bradley [3], showed that, when an acid chloride was added slowly to excess of diazomethane, the corresponding diazo ketone was formed in good yield:

$$RCOCl + CH_2N_2 \longrightarrow RCOCHN_2 + HCl.$$

They succeeded in isolating diazo ketones in the pure state, and they showed that these substances react with hydrogen chloride or bromide in ether solution with formation of the corresponding chloro or bromo ketones [3].

In the present investigation we studied the possibility of obtaining fluoro ketones by the decomposition of diazo ketones with hydrogen fluoride, the diazo ketones examined being 2-diazoacetophenone and 2-diazo-4'-nitroacetophenone.

Although benzoyl chloride was added slowly to a very large excess (tenfold in some experiments) of diazomethane solution, we did not succeed in obtaining 2-diazoacetophenone in the pure state: it always contained about 19% of the chloro ketone. In the case of p-nitrobenzoyl chloride, the corresponding diazo ketone was obtained in the completely pure state.

Study of the reaction of these diazo ketones with hydrogen fluoride showed that treatment of their solutions in absolute ether with anhydrous hydrogen fluoride gave the corresponding fluoro ketones in almost quantitative yield:

$$ArCOCHN_2 + HF \longrightarrow ArCOCH_2F + N_2.$$

The reaction must be carried out in sufficiently dilute solution, otherwise considerable resinification occurs. A stoichiometric amount of hydrogen fluoride must be taken.

EXPERIMENTAL

I. Preparation of 2-Fluoroacetophenone

1. An ethereal solution of diazomethane (2 moles) was placed in a three-necked round-bottomed flask fitted with stirrer, thermometer, and dropping funnel. The contents of the flask were stirred vigorously at below 0°, and a solution of 40 g of benzoyl chloride in 40 ml of ether was dropped in slowly. Reaction occurred with vigorous evolution of nitrogen. When the addition was complete, the mixture was left overnight at room temperature; ether was then distilled off under reduced pressure. The diazo ketone obtained contained about 19% of chloroacetophenone; it was used in further reactions without purification.

2. Anhydrous hydrogen fluoride (7.8 g) was added to a cooled solution of 16 g of commercial diazoacetophenone (containing about 3.0 g of chloroacetophenone) in 150 ml of ether. Vigorous evolution of nitrogen occurred.

Ether was distilled off under reduced pressure, and the residue was carefully fractionated. The third distillation gave a fraction of b.p. 90-91° (12 mm). The 2-fluoroacetophenone so obtained is a colorless liquid having a pleasant floral odor and no lachrimatory effect. The yield was almost quantitative. It had d_{20}^{20} 1.154, n_D^{20} 1.5200; Found MR 36.03; Calculated MR 36.45. The properties of the substance obtained coincide with those of a preparation obtained by the action of fluoroacetyl chloride on benzene [4].

Found %: C 69.6 ; H 5.2; F 12.78
C_8H_7OF. Calculated %: C 69.5; H 5.1; F 13.75

II. Preparation of 2-Fluoro-4'-nitroacetophenone

1. 2-Diazo-4'-nitroacetophenone was prepared by the above-described procedure. For 2 moles of diazomethane, 20 g of p-nitrobenzoyl chloride was taken. The 2-diazo-4'-nitroacetophenone obtained, which crystallized immediately, was filtered off and washed with 50 ml of cold ether. The preparation contained practically no chlorine, which indicated the complete absence of 2-chloro-4'-nitroacetophenone as impurity. The yield was almost quantitative.

2. Anhydrous hydrogen fluoride (1.2 g) was added to 400 ml of an ethereal suspension of 10 g of 2-diazo-4'-nitroacetophenone contained in a flask fitted with reflux condenser. Slight warming was applied (temperature not above 25–30°). Dissolution of the diazo ketone and evolution of nitrogen continued for two hours. The very small insoluble residue that remained was filtered off. Ether was distilled off under reduced pressure, and white crystals then separated, which after two crystallizations from water melted at 133°. The yield was quantitative.

Found %: C 52.8; H 3.22; N 7.70; F 10.54
$C_8H_6O_3FN$. Calculated %: C 53.0; H 3.21; N 7.73; F 10.5

SUMMARY

The reaction between anhydrous hydrogen fluoride and diazo ketones was studied. It was shown that, when treated with hydrogen fluoride, 2-diazoacetophenone and 2-diazo-4'-nitroacetophenone give good yields of 2-fluoroacetophenone and the previously unknown 2-fluoro-4'-nitroacetophenone, respectively.

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METATHETIC REACTIONS OF ACETALDEHYDE DIBUTYL ACETAL

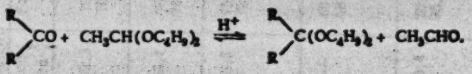
M. F. Shostakovsky, N. A. Gershtain, and V. A. Neterman

It is well known that acetals readily undergo various reactions in which alkoxy groups are exchanged for other atoms and groups under the influence of acid reagents [1-10], but there are practically no data in the literature on the exchange of the aldehydes of acetals. There is only the report by Holmberg [11] of the replacement of benzaldehyde by formaldehyde in a series of mercaptals:

$$CH_2O + C_6H_5CH(SCH_2COOH)_2 \rightarrow CH_2(SCH_2COOH)_2 + C_6H_5CHO.$$

We have studied the reactions of acetaldehyde dibutyl acetal with various aldehydes and ketones, and we have found that the main direction of reaction is the replacement of the acetaldehyde in the acetal by other aldehydes and ketones with formation of the corresponding dibutyl acetals (transacetalation):

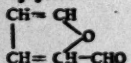
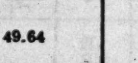
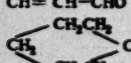
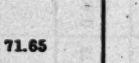
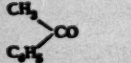
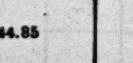
$$RCHO + CH_3CH(OC_4H_9)_2 \overset{H^+}{\rightleftharpoons} RCH(OC_4H_9)_2 + CH_3CHO;$$



Data on this reaction are given in Table 1.

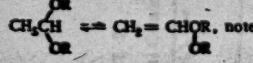
TABLE 1

Data for Transacetalation Reaction

Aldehyde	Amount (g)	Amount of acetaldehyde dibutyl acetal (g)	Acetal obtained	Yield (g)	Yield (%)
C_2H_7CHO	43.26	50.0	$C_2H_7CH(OC_4H_9)_2$	47.15	80.31
C_6H_5CHO	63.66	52.49	$C_6H_5CH(OC_4H_9)_2$	31.36	44
	49.64	43.65		25.0	44
	71.65	60.9		14.85	18.6
	44.85	29.68		1.49	4.57

Note. Acetaldehyde was partially converted into crystalline paraldehyde.

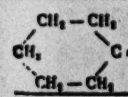
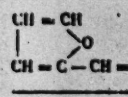
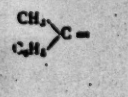
In addition, high-boiling products were formed, and the structures of these have not yet been established. The amount of acetaldehyde that separated corresponded to the amounts of the new acetals formed. The reactions studied probably have a cation-chain mechanism, which is preceded by the equilibrium state of the acetals



, noted previously [6].

TABLE 2

Physical Constants and Analytical Data for Acetals and their Derivatives

$R(OC_4H_9)_2$ R=	B.p. in °C (p in mm)			MR		Molecular weight		C (%)		H (%)		M.p. of 2,4-dinitrophenylhydrazone (°C)***
				Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	
C_6H_5CH = *	82.5—83 (3)	1.4175 20°	0.8318 20°	61.20	60.902	189.5 190.3	202.3	70.81 70.80	71.13	12.94 12.99	12.95	122.5
$C_6H_4(CH_3)CH$ = **	117.1—118.1 (1.5)	1.4751 21°	0.9315 21°	71.31	71.155	228.4 220.9	236.4	76.19 76.01	76.26	10.14 10.16	10.24	234.5
	124.8—125.6 (13)	1.4445 18.5°	0.8934 18.5°	68.04	67.938	212.5 211.4	228.3	73.40 73.58	73.60	12.19 12.27	12.35	204.0
	95—95.2 (3)	1.4485 20°	0.94556 20°	64.133	64.029	—	—	69.08 68.90	68.98	9.68 9.70	9.80	157.2
	113—115 (3)	1.4865 18.5°	0.9443 18.5°	76.12	75.773	231.1 229.7	250.4	76.83 76.90	76.76	9.78 9.80	10.17	241.7—241.8

* The literature [12, 13] gives: b.p. 97-98° (10 mm); n_D^{20} 1.4160; b.p. 212-214° (760 mm); 84-86° (8 mm); n_D^{18} 1.4190.

** The literature [14] gives: b.p. 155-156° (20); n_D^{20} 1.4770; d_4^{20} 0.935.

*** In the reaction between benzaldehyde and acetaldehyde dibutyl acetal, a product having the following properties was isolated: b.p. 153-154° (mm); n_D^{20} 1.4906; d_4^{20} 0.9789; M 306.8, 306.1; %C 75.72; 75.90; %H 9.43; 9.39; We have not yet established its structure.

EXPERIMENTAL*

The preparation was carried out in a three-necked flask fitted with mechanical stirrer and reflux condenser. The aldehyde or ketone and acetaldehyde dibutyl acetal (the constants of which corresponded to data in the literature for the chemically pure substances) were taken in the molar ratio of 2:1; the catalyst was concentrated hydrochloric acid (0.5-1.0% on the total mass of the substances). The mixture was heated with constant stirring at about 70-100° for 3-4 hours and was then set aside for 12-24 hours. The acetaldehyde that separated was blown out of the system with a current of dry nitrogen and was trapped in coiled receivers cooled with dry ice in acetone (these were connected to the reflux condenser). The reaction products were vacuum-fractionated in a current of dry nitrogen. The low-boiling fractions consisted of unchanged aldehyde or ketone and acetaldehyde dibutyl acetal. After the first fractionation, the required acetal was treated with sodium and redistilled. The structures of the acetals formed were proved by the preparation of 2,4-dinitrophenylhydrazones, the melting points of which agreed with the literature data cited by Heilbron and Bunbury [15]; mixture tests showed no melting point depression. The constants and analytical data for the compounds obtained and their derivatives are given in Table 2.

We thank I. I. Zaretskaya for kindly supplying the 2,4-dinitrophenylhydrazones for the mixture tests.

SUMMARY

1. It was shown that, when aldehydes and ketones were treated with acetaldehyde dibutyl acetal, a transacetalation reaction occurred.

2. By this method the following compounds were synthesized from acetaldehyde dibutyl acetal: the dibutyl acetals of butyraldehyde, benzaldehyde, 2-furaldehyde, cyclohexanone, and acetophenone.

3. It was shown that this reaction is an equilibrium process and can be extended to the transacetalation of various acetals of a great variety of aldehydes and ketones.

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* Laboratory worker R. Ya. Egorova took part in the experimental work.

** T. p. = C. B. Translation pagination.

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CURRENT EVENTS

CHEMICAL CONFERENCES IN THE GERMAN FEDERAL REPUBLIC

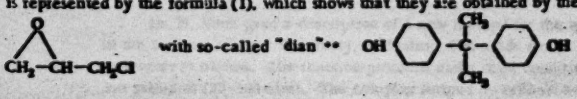
I. ANNUAL MEETING OF THE GERMAN SOCIETY FOR THE INVESTIGATION OF FATS*

The annual meeting of the German Society for the Investigation of Fats was held on September 25-30, 1955, at Münster (Westphalia). In the program of the meeting the main attention was directed to natural fats and various products prepared from them. The following fundamental papers were read: "Oxidative Changes in Fats", "Edible Fats", "New Methods of Analysis for Fats and Substances prepared from them", "Technology of the Treatment of Fats — Machines and Apparatus", etc. There were also papers, which we shall list below, on synthetic material and methods for their preparation and analysis. The papers were read at two simultaneous sessions: 1) soaps and detergents, and 2) paints. The texts of the papers are published in the journal "Fette, Seifen, Anstrichmittel" in the issues of late 1955.

The papers read at the first session were: 1) P. Ommert (Marl) "Infrared Spectroscopy of Alkane- and Alkenesulfonates"; 2) J. Pfefferkorn (Münster) "The Electron Microscope and the Scope of its Application"; 3) W. Kling (Düsseldorf) "The Electron Microscope in the Analysis of Detergents"; 4) K. Pott (Stuttgart) "Practical Experience of Paper Chromatography in the Soap Field"; 5) M. Loury (Paris) "Methods of Calculating the McBain Diagram; 6) A. Petrov (Moscow) "Catalytic Polymerization of Propene"; 7) F. Wolbert (Münster) "Ultraviolet Spectroscopy of Alkylarenesulfonates and Sulfuric Esters of Fatty Alcohols"; 8) H. Thomas (Holzminden) "New Syntheses of Azulenes and their Application in Cosmetics".

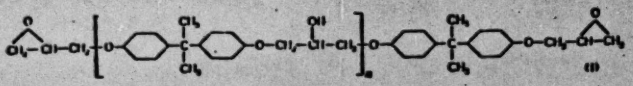
The papers read at the second session were: 1) A. Seger (Münster) "Stagewise Hydrogenation of Polyalkynoic Acids"; 2) R. Milewski (Bochum) "Emulsions of Styrene-Butadiene Copolymers as Lacquers"; 3) H. Kaufmann and E. Gulinsky (Münster) "Electron Microscopy in the Paint Field"; 4) L. Korfhage (Hamburg) "New Developments in Epoxy-Resin Paints"; 5) H. Kaufmann and E. Gulinsky (Münster) "Automatic Recording of the Changes in Weight of Drying Paints. Porphine as a Diseccant"; 6) H. Kaufmann and H. Kirschnek (Münster) "Chlorides of Polyenic Acids and Polyenic Aldehydes".

After the meeting — from September 30 to October 3 — there was a practical seminar. The participants of the seminar were able to make themselves familiar with methods of microanalysis in the fat and detergent field, the determination of iodine and thiocyanogen values, methods of chromatography and the evaluation of the efficiency of detergents, methods for the automatic determination of the oxygen absorption of drying oils, rheological methods (viscometry and consistometry), electrometric methods (polarographic determination of antioxidants and the potentiometric determination of acid values), and optical methods (methods of spectroscopy and electron microscopy). Among the lectures that were given we will refer only to that of L. Korfhage on a very promising new type of paint medium. Epoxy resins have recently begun to be manufactured in large amounts. In Europe they are known under the trade name of "Epikotes", and in America under the name of "Epons". Their structure is represented by the formula (I), which shows that they are obtained by the condensation of epichlorohydrin



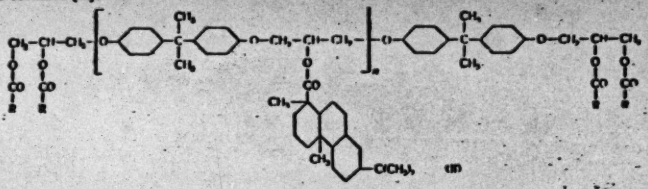
* This society (President, Prof. H. P. Kaufmann, Münster; Vice-President, Prof. G. Jacini, Milan) has now been transformed into an international society, and in view of this the next annual meeting (1956) will be held in Milan.

** This name was given in honor of one of A. Borodin's students, A. P. Dianin, who was the first to prepare this compound by the condensation of phenol with acetone.



(I)

Epikotes are readily esterified, both by fatty acids, such as the acids derived from castor, soybean, and other drying oils, and also by acids derived from nondrying oils, such as coconut oil and hydrogenated castor oil. They can be esterified also with mixtures of a fatty acid and abietic acid. The esterified Epikote resin can be represented by the formula (II).



(II)

II. Annual Meeting of the German Society for the Investigation of Petroleum and Coal Chemistry

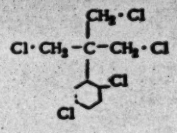
The annual meeting of the society (president, Prof. K. Ziegler, Director of the Institute of Coal Chemistry, Mülheim) took place on October 6-8, 1955. There were five plenary and thirty-one sectional papers (read at two simultaneous sessions: coal and petroleum). Interesting papers were read by Prof. C. Padovani (Milan), who has this year been given the highest award of the Society – the Karl Engler Medal, Prof. E. Terres (Karlsruhe), Dr. H. Koch (Mülheim), and Prof. G. Hugel (Paris). Prof. C. Padovani outlined the development of the chemical treatment of fuel in Italy during the last twenty years. In the meeting of demands for thermal and electrical energy, the importance of solid fuel – home-produced low-calorific coal and imported coal – is gradually diminishing owing to increased utilization of natural gases and hydroelectric energy. More than 50% of the imported coal consists of high-quality coking and gas coals. The petroleum-refining industry, according to the speaker, has developed greatly in postwar years and is now in a very satisfactory state. The petrochemical industry is also growing. In one single petroleum-treating plant, 30,000 tons of gaseous olefins are produced anually and are then converted into various chemical products. Apart from its use as a source of energy, natural gas is being used in ever-increasing quantities for the synthesis of ammonia, methanol, and acetylene and its derivatives.

Prof. E. Terres's paper was devoted to adiabatic ignition temperatures and rates of oxidation of hydrocarbons of various structure. It was shown that the difference in ignition temperature between normal and branched hydrocarbons is only slight. The difference in the detonation stabilities of these hydrocarbons is to be explained entirely by their rates of oxidation. In the case of normal hydrocarbons, there is a rapid rise in oxidizability with increase in the length of the chain. The oxidation rates of detonation-stable branched paraffins are very low. There are other causes for detonation in a diesel engine. Detonation is here determined by the presence of two separate burning regions. One is the region of homogeneous mixtures of hydrocarbon paper and air. The other is the region of supersaturated fuel vapor and air, and it is in this that rapid combustion occurs.

Dr. H. Koch gave a description of a new method for the synthesis of fatty acids that has been developed in the Institute of Coal Chemistry, Mülheim. The acids are synthesized by the addition of carbon monoxide and water to olefins. The reaction proceeds under mild conditions: at low temperatures (0-30°) and relatively low pressures (30-100 atm). The complex formed by sulfuric acid with boron trifluoride is used as catalyst. It is essential to begin by reaction with carbon monoxide in absence of water, and then to add water. The reaction has been carried out with olefins from C_3 to C_{20}, but it goes particularly well with branched olefins: the dimer and trimer of isobutene and the tetramer of propene. An interesting starting material is oleic acid, which gives a dibasic acid containing 19 carbon atoms (nonylsebacic acid). This reaction is clearly a simplification and development of W. Reppe's reaction *, by which it was proposed to synthesize acids from olefins, carbon monoxide, and water at 230-250° and 200-300 atm over the catalysts nickel carbonyl or nickel carbonyl and nickel iodide.

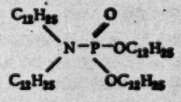
* W. Reppe, Copenhaver, Bigelow, Acetylene and Carbon Monoxide Chemistry, N.Y., 1949, p. 265.

In his paper "Effect of Catalytic Processes on the Properties and Application of Lubricating Oils", Prof. Hugel devoted his main attention to sulfur compounds – both to their negative action (corrosion, poisoning of hydrogenating catalysts), and to their positive action (inhibiting action, with respect to acids of the lubricant, of mechanisms operating under severe conditions). It was established that the formation of a layer of metal sulfide that effects lubrication depends to a certain extent on the nature of the radicals of the sulfur compounds. Sulfur is particularly reactive when it is attached to allyl or benzyl: $CH_2=CH-CH_2-S$, $C_6H_5-CH_2-S$. Some chloro derivatives have a similar action to that of sulfur compounds, e.g. 1,4-dichloro-2-(2-chloro-1,1-bischloromethylethyl)benzene



A still greater effect is obtained by the simultaneous use of sulfur and chloro compounds, e.g. by addition to the oil of 2% of "dibenzylglycol xanthate" and 4% of 1,4-dichloro-2-(2-chloro-1,1-bischloromethylethyl)benzene. The widely used graphite and molybdenum sulfide have the disadvantage that the lubricant must be applied as a suspension, which is not always stable.

The author concluded that the lubricant must be soluble in hydrocarbons, it must be stable at medium temperatures and pressures, and at high temperatures and pressures the lubricant should decompose, and must leave a solid layer on the surface of the metal which ensures that lubrication will occur. These requirements can be satisfied only by complex metal compounds, particularly such compounds of molybdenum that decompose with separation of molybdenum sulfide. However, the synthesis of complex molybdenum compounds that are soluble in hydrocarbons is not a simple matter. The author has succeeded in solving this problem in different ways. It was established that it is not essential to introduce the required sulfur into the complex: it can be dissolved in the oil in the form of an active sulfur compound. In that case, instead of molybdenum sulfide, the oxides can be taken (molybdenum blue). There are forms of these oxides that are soluble in ether and butyl alcohol, but, until now, no preparations of molybdenum oxides were known that were soluble in hydrocarbons. It was shown that, when a higher alcohol, e.g. dodecyl, is added to a butyl alcohol solution of molybdenum blue and the butyl alcohol is then removed under reduced pressure, a form of molybdenum blue is obtained that is soluble in hydrocarbons. Molybdenum blue can be combined also with phosphoric acid. If, instead of phosphoric acid, we take a hydrocarbon-soluble derivative, e.g. (III)



(III)

and combine it with molybdenum blue, we again obtain a complex molybdenum compound that is soluble in oils. The corresponding derivative of phosphorothionic acid can also be taken, and it is then no longer necessary to introduce any other sulfur compound into the oil.

The program of the conference included a visit to Ludwigshafen. Seventy of the participants took part in the visit, but it was not possible for each of these to see what interested him. No meeting with W. Reppe and K. Pier was arranged. The affair was limited to an excursion around the works, a lecture on the origin of the firm, the showing of a film relating to works reconstruction after the war, and an inspection of two old production departments – for Carbide dyes and for Indanthren dyes.

The papers read at the conference in Karlsruhe are being published in Erdöl and Kohle and in Brennstoff-Chemie. I take this opportunity of passing on to Soviet chemists the invitation of the editorial boards of Fette, Seifen, Anstrichmittel and of Erdöl and Kohle to contribute to these journals, to which the chemists of France, Holland, Hungary, the German Democratic Republic, and other countries already contribute.

A. D. Petrov
Corresponding Member of the Academy of Sciences of the USSR

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To NIKOLAI NIKOLAEVICH SEMENOV

Dear Nikolai Nikolaevich:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, warmly congratulate you on the attainment of the age of sixty and the completion of forty years of scientific, pedagogical, and organizational activities.

Your name will always be associated with outstanding discoveries relating to chemical chain reactions and to the processes occurring during combustion, explosion and flame propagation. In your person, we salute also one who has long served as the Director of a leading Institute of the Division, the Institute of Chemical Physics of the Academy of Sciences of the USSR - a position in which you have shown outstanding initiative.

We hope, dear Nikolai Nikolaevich, that further great successes lie before you in all fields of your activity, and we wish you health and vigor in your creative labors.

Division of Chemical Sciences of the
Academy of Sciences of the USSR
and
Editorial Board of the Bulletin of
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Division of Chemical Sciences

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KINETICS OF THE OXIDATION OF ACETALDEHYDE BY PEROXYACETIC ACID

R. F. Vasil'yev and N. M. Emanuel

Processes of oxidation with molecular oxygen belong to a class of chemical reactions that have a complicated mechanism. It was for this class of reactions that A. N. Bakh and K. Engler developed, in a particularly clear form, the concept of the important parts played by intermediate products and stages in chemical transformations. A new stage in the development of the theory of oxidative processes is associated with the introduction of the concept of a chain mechanism in these reactions. N. N. Semenov formulated the theory of degenerate branching, according to which peroxy compounds formed in the course of the reaction break down from time to time into radicals, which initiate new oxidation chains. This theory enables us to understand the slowness and autoacceleration of reactions between organic substances and molecular oxygen.

There can be no doubt that the direct oxidation of the substance by a peroxy compounds, i. e. by combined oxygen, is also worthy of attention. Such processes can occur both in systems in which oxidation by molecular oxygen is proceeding and the peroxy compounds is formed as an intermediary, and also in systems in which molecular oxygen is absent. The elucidation of the kinetics and mechanisms of processes of this kind presents much scientific and practical interest.

This paper is concerned with a study of the kinetics of the oxidation of acetaldehyde by peroxyacetic acid. In our choice of subject for investigation we were guided by the following considerations: a) reaction between an aldehyde and a peroxy acid is known to be one of the stages in the complex process of the oxidation of an aldehyde by molecular oxygen; b) the system aldehyde–peroxy acid is in itself a convenient model for the study of the kinetics and mechanism of oxidation by combined oxygen, for this process occurs comparatively readily and the number of reactants and products is small.

EXPERIMENTAL

Peroxyacetic acid was prepared from highly concentrated hydrogen peroxide and acetic anhydride by d'Ans and Frey's method [1]. The peroxyacetic acid content of the product was 70-82%, the remainder being acetic acid. It was kept at the temperature of dry ice (−78°) in a vessel having a ground-in stopper. It was shown that, when kept in this way, peroxyacetic acid does not undergo appreciable decomposition in the course of several months. The acetaldehyde solution was prepared from commercial acetaldehyde, which was dried over calcium chloride and distilled in a current of nitrogen into a vessel containing solvent. A freshly prepared solution was used on each occasion. Solvents were first distilled twice through a fractionation column. The cylindrical reaction vessels (diameter 15 mm, height 140 mm) were provided with ground-in stoppers and side arms through which nitrogen was passed in order to provide an inert atmosphere. In the temperature range 0° to −40°, a Dewar vessel containing acetone cooled with small portions of dry ice was used as a thermostat, constancy of temperature being maintained within ±0.3°. In the range 15-40°, a Heppler ultrathermostat, constant within ±0.03°, was used, and for experiments at 0° the reaction vessel was immersed in a Dewar vessel filled with melting ice.

Before a series of experiments, stock solutions of acetaldehyde and perox acetic acid were prepared. A definite amount (usually 10 ml) of the acetaldehyde solution was introduced into the reaction vessel immersed in the thermostat. When this solution had attained the temperature of the thermostat, a measured amount (usually 1-2 ml) of the peroxyacetic acid solution, also brought to the temperature of the thermostat, was added. The moment at which mixing occured was taken as the beginning of the reaction. Tests for chemical analysis were taken with a 0.36 ml thin-walled pipet. The concentration of peroxyacetic acid and peroxy product was determined by Kagan and Lyubarsky's method. Acetaldehyde was determined by titration of the hydrochloric acid liberated when the aldehyde reacted with hydroxylamine hydrochloride. A special method was developed for determining the acetic acid concentration. Experiments with artificial mixtures showed that, if the test samples were diluted with water, oxidation of aldehyde by peroxy acid continued during the analysis, and the values obtained for the acetic acid concentration were too high. We therefore diluted the test samples with potassium iodide solution. The peroxy acid was then immediately destroyed with liberation of iodine, and oxidation of the aldehyde was stopped. A definite volume of standard sulfuric acid was then added from a microburet, and iodine was titrated with thiosulfate solution. The total amount of acid was then titrated to phenolphthalein with alkali.

From the equation of the analytical reaction

$$CH_3COOOH + 2KI + H_2SO_4 = CH_3COOH + I_2 + K_2SO_4 + H_2O$$

and from the condition that the total amount of acid must be equal to the amount of alkali required in the titration, it is easy to determine the amount of acetic acid removed from the reaction vessel:

$$(CH_3COOH) = (OH^-)_{titr} - (H_2SO_4) + (CH_3COOOH)$$

in which (CH_3COOH) is the amount of acetic acid in the sample, $(OH^-)_{titr}$ is the amount of alkali required in the titration, and (CH_3COOOH) is the amount of peroxyacetic acid in the sample (all amounts are expressed as volumes of solutions of identical normality).

Theoretical and Experimental Kinetic Laws of the Reaction

It is known that the oxidation of aldehydes by peroxy acids results in the formation of carboxylic acids:

$$RCHO + RCOOOH \rightarrow 2RCOOH. \qquad (1)$$

Several workers (Kagan and Lyubarsky [2, 3], Bawn and Williamson [4], Meerwein and Bodendorf [5], who have studied these reactions, have shown that in the course of the oxidation process a new peroxy compound is formed and then disappears again, this compound being in equilibrium with the original reactants. Treating this compound as an intermediate product, they assumed the following scheme of reaction:

$$RCHO + RCOOOH \underset{k_3}{\overset{k_1}{\rightleftarrows}} Y \xrightarrow{k_2} 2RCOOH, \qquad (2)$$

in which Y is the intermediate peroxy compounds, and k_1, k_2, and k_3 are rate constants.

However, the observed behavior of the peroxy compounds cannot in itself serve as an unequivocal proof of the mechanism (2). The formation and subsequent decomposition of the new compound can be explained on the basis of a completely different mechanism, in which the acid is formed directly from the aldehyde and peroxy acid and the new peroxy compound is not an intermediary, but a by-product:

$$\begin{cases} RCHO + RCOOOH \underset{k_3}{\overset{k_1}{\rightleftarrows}} Y; \\ RCHO + RCOOOH \xrightarrow{k_2} 2RCOOH. \end{cases} \qquad (3)$$

This second possibility was not envisaged by the authors of these papers, although their experimental data agreed equally well with both of the mechanisms (2) and (3). Hence, the very likely hypothesis of a stagewise mechanism for the process was not provided with the necessary experimental proof.

However, the mechanisms (2) and (3) differ fundamentally, and it would be expected that the kinetics of the process would also be different. We have examined theoretically the character of the kinetic laws corresponding to the mechanisms (2) and (3) in order to find distinguishing features that would make it possible to make a choice between these two alternative reaction schemes. The simplest method for making such an examination consisted in assuming reaction laws of a simple type (first and second order) for the kinetics of the separate stages. Comparison of the results of the theoretical analysis with experiment fully justifies this assumption.

The mechanisms (2) and (3) correspond to the following systems of differential equations:

$$\begin{cases} \frac{d}{dt}(CH_3COOOH) = \frac{d}{dt}(CH_3CHO) = -k_1(CH_3COOOH)(CH_3CHO) + k_3(Y); \\ \frac{d}{dt}(Y) = k_1(CH_3COOOH)(CH_3CHO) - (k_2 + k_3)(Y); \\ \frac{d}{dt}(CH_3COOH) = 2k_2(Y). \end{cases} \qquad (4)$$

$$\begin{cases} \frac{d}{dt}(CH_3COOOH) = \frac{d}{dt}(CH_3CHO) = -(k_1 + k_3)(CH_3CHO)(CH_3COOOH) + k_2(Y); \\ \frac{d}{dt}(Y) = k_1(CH_3COOOH)(CH_3CHO) - k_2(Y); \\ \frac{d}{dt}(CH_3COOH) = 2k_3(CH_3COOOH)(CH_3CHO). \end{cases} \quad (5)$$

We could not obtain exact solutions of these equations because they are not linear. An approximate solution can be obtained on the assumption that one of the reactants (aldehyde) is in excess with respect to the other (peroxy acid). The equations then reduce to linear forms, and solutions are obtained as follows:

a) in the case of mechanism (2)

$$x = \frac{1}{m_2 - m_1}\left\{(m_2 - \alpha)e^{-m_1\tau} - (m_1 - \alpha)e^{-m_2\tau}\right\}. \quad (6)$$

$$y = \frac{\alpha}{m_2 - m_1}\left\{e^{-m_1\tau} - e^{-m_2\tau}\right\}. \quad (7)$$

$$z = 1 - \frac{1}{m_2 - m_1}\left\{m_2 e^{-m_1\tau} - m_1 e^{-m_2\tau}\right\}. \quad (8)$$

b) in the case of mechanism (3)

$$x = \frac{1}{l_2 - l_1}\left\{(1 - l_1)e^{-l_1\tau} - (1 - l_2)e^{-l_2\tau}\right\}. \quad (9)$$

$$y = \frac{\alpha}{l_2 - l_1}\left\{e^{-l_1\tau} - e^{-l_2\tau}\right\}. \quad (10)$$

$$z = 1 - \frac{1}{l_2 - l_1}\left\{(l_2 - \gamma)e^{-l_1\tau} - (l_1 - \gamma)e^{-l_2\tau}\right\}, \quad (11)$$

in which x, y, and z are concentrations of components relative to the initial concentration of peroxyacetic acid:

$$x = \frac{(CH_3COOOH)}{(CH_3COOOH)_0}; \quad y = \frac{(Y)}{(CH_3COOOH)_0}; \quad z = \frac{(CH_3COOH)}{2(CH_3COOOH)_0}; \quad (12)$$

the values of α, β, γ, and τ are defined by the expressions:

$$\alpha = \frac{k_1}{k_3}(CH_3CHO)_0; \quad \beta = \frac{k_2}{k_3}; \quad \gamma = \frac{k_2}{k_3}(CH_3CHO)_0; \quad \tau = k_3 t; \quad (13)$$

$-m_1$, $-m_2$, $-l_1$, and $-l_2$ are roots of the characteristic equations:

$$m^2 + (1 + \alpha + \beta)m + \alpha\beta = 0 \text{ and } l^2 + (1 + \alpha + \gamma)l + \gamma = 0.$$

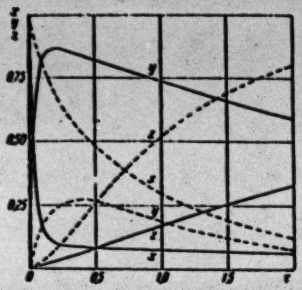


Fig. 1. Theoretical kinetic curves corresponding to the mechanism (2) constructed according to Equations 6, 7, and 8; x, y, and z are the relative concentrations of peroxyacetic acid, intermediate peroxy compound, and acetic acid, respectively. The curves are plotted for the following values of the parameters: ——— $\alpha = 10$, $\beta = 0.1$; – – – – $\alpha = 1$, $\beta = 1$.

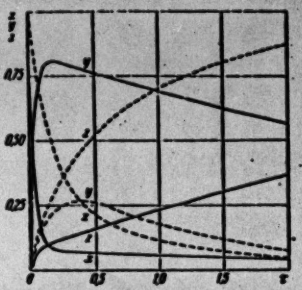


Fig. 2. Theoretical kinetic curves corresponding to the mechanism (3) constructed according to Equations 9, 10, and 11; x, y, and z are the relative concentrations of peroxyacetic acid, by-product peroxy compound, and acetic acid, respectively. The curves are plotted for the following values of the parameters: ——— $\alpha = 10$, $\gamma = 1$; – – – – $\alpha = 1$, $\gamma = 1$.

By way of example, Figures 1 and 2 give the theoretical kinetic curves plotted according to Equations 6-8 and 9-11 respectively, definite values being taken for the parameters α, β, and γ [i.e. so that definite relationships exist between the constants k_1, k_2, and k_3 and the concentration $(CH_3CHO)_0$]. As will be seen from Figures 1 and 2, the kinetic curves for peroxyacetic acid and the peroxy intermediary or by-product are qualitatively alike in the two cases. A qualitative difference in the form of the kinetic curves is found only for the final product, acetic acid. In the case of the mechanism (3) the acid accumulates according to a curve of a simple type, but in the case of the stagewise mechanism (2) the kinetic curve for the final product has an autocatalytic form. As can be readily shown by calculation, the inflection on the curve occurs at the point at which not more than 26% conversion has been attained.

The curves for the accumulation of acid coincide with the kinetic curves for the fall in the overall amount of active oxygen, i. e. the oxygen present both in the form of peroxy acid and peroxy intermediary or by-product, as follows from the general balance of the reactions in the stoichiometric equations (2) and (3). A comparison of the kinetic curves in Figures 1 and 2 leads to the conclusion that a choice between the mechanisms (2) and (3) can be made only on the basis of a study of the kinetics of the formation of acetic acid or the kinetics of the overall loss of active oxygen.

It is interesting to note that in investigations devoted to the oxidation of aldehydes by peroxy acids, the kinetics of acid formation have received practically no study. The paper of Bawn and Williamson [4] gives data on the overall loss of active oxygen in the reaction between acetaldehyde and peroxyacetic acid. The authors favor the concept of an intermediate stage [mechanism (2)]. Unfortunately, the number of experimental points is not sufficient for the course of the curve to be followed in detail, and the overall loss of active oxygen is represented by a curve of a simple type. Wittig and Pieper [6] studied the kinetics of the formation of benzoic acid and the consumption of peroxybenzoic acid in the oxidation of benzaldehyde. The kinetic curves given in the paper are of the simple type. However, the absence of experimental points on the kinetic curves makes it impossible for us to judge the accuracy to which the form of the curves was established. Thus, the experimental data presented by these authors corresponds most closely to the mechanism (3), in spite of the fact that they consider that the reaction proceeds by the stagewise mechanism (2).

Essentially, therefore, the question of the mechanism of the reaction and the part played in it by the

peroxy compound formed during the reaction remains unresolved. We have therefore made a special study of the kinetics of the formation of acetic acid. The experiments were carried out in toluene solution at close to room temperature. Most of the experiments were carried out with an 8 to 15-fold excess of aldehyde with respect to peroxy acid, i.e. under the conditions under which Equations 6-11 are valid.

Figures 3 and 4 give the results of our study of the kinetics of the formation of acetic acid and the kinetics of the diminution in the sum of the concentrations of peroxyacetic acid and the peroxy product (i.e. in the overall concentration of active oxygen). It will be seen from these curves that the experimental points characterizing the two relationships are almost in coincidence. This coincidence of the two relationships enables us to use two sets of experimental data obtained independently of one another for the construction of a single kinetic curve, so that the form of this curve can be established with greater accuracy.

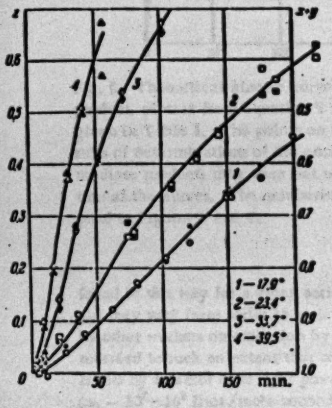


Fig. 3. Kinetics of the formation of acid (left scale, black points) and of the diminution in overall concentration of peroxy compounds (right scale, white points) in toluene solution. Initial concentrations: aldehyde 1.29 moles/liter, peroxy acid 0.10 mole/liter. Curves plotted from Equation 8.

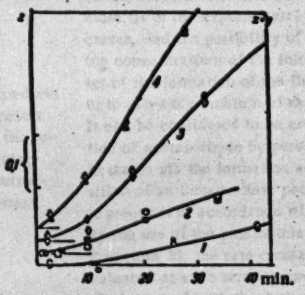


Fig. 4. Initial sections of the kinetic curves in Fig. 3. The curves have been displaced to different extents along the axis of ordinates; the scale for the measurement of degree of conversion is indicated. The numbering and signs correspond to Fig. 3.

TABLE 1

Experiment No.	Temperature °C	α	β	$k_2 \cdot 10^4$ (sec^{-1})
1	17.9	12.0	0.6	0.99
2	23.4	9.8	0.8	1.1
3	33.7	7.1	0.9	2.6
4	39.5	5.8	1.1	3.8

As will be seen from Fig. 4, the formation of acetic acid proceeds with initial acceleration. A qualitative examination of the curves for the formation of acid therefore supports the mechanism (2). The curves in Figures 3 and 4 were plotted from Equation 8, being fitted to the experimental points by suitable choice of the parameters α, β, and k_2. Calculation of k_2 was based on a simple transformation of the kinetic curves by a change in the scale of the time axis. The parameter k_2, therefore, does not affect the form of the curve. The parameter $\alpha = \frac{k_1}{k_2}(CH_3CHO)_0 = \frac{(CH_3CHO)_0}{K}$ depends on the initial acetaldehyde concentration and the value of the equilibrium constant. The latter was determined in independent experiments (see below). The parameter α, therefore, was known beforehand. The parameter β was found by selecting a value that resulted in satisfactory fitting of the theoretical curve to the experimental points.

Table 1 gives the values of the parameters for the four experiments of this series, which were carried out at different temperatures.

The data in Table 1 in conjunction with Equation 7 can be used also for the construction of theoretical

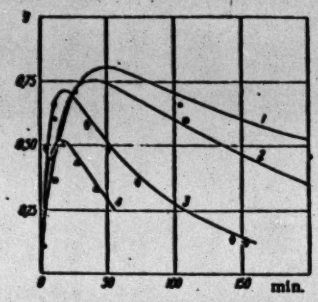


Fig. 5. Theoretical kinetic curves for the intermediate product, plotted from Equation 7 with the parameters given in Table 1. The points on the curves are the results of determinations of the concentration of intermediate product; they were not used for the construction of the curves. The numbering and signs correspond to Figures 3 and 4.

curves for the intermediate product. These curves are shown in Fig. 5. The points distributed along the curves represent the results of special determinations of the concentrations of the intermediate product in the respective experiments; they were not used for the construction of the curves. In all cases the fitting of the experimental points to the theoretical curves is quite satisfactory. This result provides a quantitative proof of the correctness of the mechanism (2).

Thus, the qualitative form of the kinetic curve for the formation of acid (initial acceleration), the close fit of the experimental points to the theoretical curves, and the possibility of calculating the changing concentrations of the intermediary from the kinetics of the formation of the final product have enabled us to solve the problem of the reaction mechanism. It can be considered to be established that the oxidation of acetaldehyde by peroxyacetic acid proceeds in stages via the formation and subsequent decomposition of an intermediate peroxy compound; i.e. that it proceeds in accordance with the mechanism (2). By the use of the parameters given in Table 1 and Equations 13, the rate constants k_1 and k_3 can be evaluated at each temperature. The rate constants found in this way for a given series of experiments are closely in accord with the Arrhenius law $k = ae^{-E/RT}$, but they vary from series to series. Unsatisfactory reproducibility of the values of rate constants has been noted by other workers on oxidation by peroxy acids [7]. In particular, the reaction of acid formation is sometimes retarded to such an extent that only the first stage is realized for practical purposes. The preexponential factor is less by a factor of several powers of ten than the usual values of about 10^{11} liter/mole·second or 10^{13} second^{-1} ($a_1 \sim 10^2 - 10^5$ liter/mole·second, $a_3 \sim 10^5 - 10^8$ second^{-1}, and $a_3 \sim 10^8$ second^{-1}), so that they cannot be treated within the framework of the usual collision theory for bimolecular reactions or in terms of bond-vibration frequencies in the case of unimolecular reactions. Moreover, the activation energies of the individual stages ($E_1 \sim 7, E_2 \sim 13, E_3 \sim 17$ kcal/mole) are very much less than the values characteristic for reactions between saturated molecules (several tens of kilocalories [8]).

The detailed mechanism of the reaction studied is probably more complex than that indicated in the overall scheme (2). It is possible that a chain reaction occurs. The experimentally determined rate constants may then be related in a complex manner with the constants for the elementary processes. For this reason, both the preexponential factors and the activation energies, which are combinations of the corresponding characteristics of the elementary stages, may differ substantially from the usual values *.

It must again be emphasized, however, that the chemical mechanism (2) closely represents the kinetics of the overall reaction and leads to conclusions that are in accord with the laws found experimentally. These laws are as follows:

1. The kinetics of the formation of acetic acid and the diminution in total active oxygen are described by Equation 8, the point of inflection occurring at about 25% conversion.

2. The concentration of the intermediate product varies with time in accordance with Equation 7. The fact that suitable treatment of data on the kinetics of formation of the final product enables to calculate correct-

* There is another possible cause for the low value of the preexponential factor for the reaction resulting in the formation of the intermediate product - the low steric factor ($10^{-3} - 10^{-5}$) associated with addition reactions.

TABLE 2

Temp. (°C)	Concentration* (mole/liter) $(CH_3CHO)_0$	$(CH_3COOH)_0$	$(CH_3COOH)_\infty$	K (mole/liter)
−20	0.0948	0.0313	0.0013	0.028
−20	0.330	0.436	0.0038	0.025
0.0	0.281	0.0370	0.0000	0.052
0.0	0.330	0.0475	0.0072	0.053
0.0	0.330	0.0436	0.0076	0.061
+19.3	0.284	0.0370	0.0122	0.128
+19.3	0.281	0.0370	0.0112	0.113
+20.1	0.330	0.0475	0.0139	0.122
+30.4	0.330	0.0436	0.0165	0.187

* The values of concentration correspond to 20°. In the calculations the dependence of the density of toluene on temperature was taken into account.

ly the kinetic curves for the intermediate product shows that we may exclude the possibility that this peroxy compound is actually a by-product and that the initial acceleration on the kinetic curve for the acid is due to the complex mechanism by which it is formed from the original reactants. It will be clear that, if this were true, there would be no correlation between the two processes indicated above.

3. The rate constants obey the Arrhenius law, and the temperature coefficient for the formation of acid is greater than that for the formation of the intermediate peroxy compound. Experiment shows that there is a powerful temperature effect associated with the retardation of the second stage. Thus, at low temperatures, (−40-0°) practically no acetic acid is formed, and the reaction consists only in the establishment of the equilibrium:

$$CH_3CHO + CH_3COOOH \rightleftharpoons Y.$$

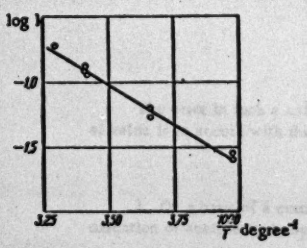


Fig. 6. Equilibrium constant for the formation of intermediate product as a function of temperature.

4. The rate of formation of the intermediate product is proportional to the product of the concentrations of peroxy acid and aldehyde. That the reaction is of first order with respect to the peroxy acid follows from the applicability of Equations 6-8 in the description of the kinetics of the process. As the aldehyde was in excess in the above-described series of experiments, special experiments were carried out at lower concentrations. When the acetaldehyde concentration was changed by a factor of six, the bimolecular constant k_1 changed by only 6%, which indicated a first-order reaction with respect to aldehyde concentration. It is probable that, in this reaction, we are dealing with a complex process that simulates a simple one having simple kinetic laws.

We also obtained confirmation of the suggestion made by other authors [2-4] that an equilibrium exists between the intermediate peroxy compound and the original reactants. The equilibrium constant was determined in those experiments in which the stage of acetic acid formation was retarded. The experiments were carried out in toluene solution.

Table 2 gives the data for, and the results of, the calculation of equilibrium constants from the formula:

$$K = \frac{k_2}{k_1} = \frac{(CH_3CHO)_{eq}\,(CH_3COOOH)_{eq}}{(Y)_{eq}} =$$

$$= \frac{(CH_3CHO)_0 - (CH_3COOOH)_0 + (CH_3COOOH)_{eq}}{(CH_3COOOH)_0 - (CH_3COOOH)_{eq}} \cdot (CH_3COOOH)_{eq},$$

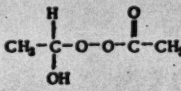
in which ( )$_0$ indicates initial concentrations and ( )$_{eq}$ indicates final concentrations (at the equilibrium state).

A linear relationship is found between the logarithm of the equilibrium constant and the reciprocal of the temperature (Fig. 6), and this permits us to write the following expression for the equilibrium constant:

$$K = 1.6 \cdot 10^5 \cdot e^{-\frac{5500}{RT}} \text{ mole/liter.}$$

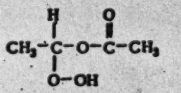
The formation of the intermediate product is therefore accompanied by the evolution of 5.5 kcal/mole. Estimates of heat of reaction on the basis of mean bond energies give the following values for structures suggested in the literature for the intermediate peroxy compound:

I. 1-Hydroxyethyl peroxyacetate (Wieland [9], Kagan and Lyubarsky [2, 3]):



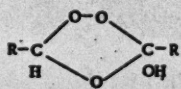
$Q_{calc} = -10$ kcal/mole

II. 1-Hydroperoxyethyl acetate (Bawn and Williamson [4]):



$Q_{calc} = -10$ kcal/mole

III. An isoozonide (Wittig and Pieper [6]):



$Q_{calc} = -20$ kcal/mole

The error in such a calculation is of course large, and it may therefore be considered that the experimental value is in accord with the theoretical estimate.

SUMMARY

1. On a basis of a comparison of the theoretical and experimental kinetic laws it was shown that the oxidation of acetaldehyde by peroxyacetic acid proceeds in two stages:

a) reversible formation of an intermediate peroxy compound:

$$CH_3CHO + CH_3COOOH \rightleftharpoons Y,$$

b) decomposition of the intermediate compound into the final product, acetic acid:

$$Y \rightarrow 2CH_3COOOH.$$

2. A study was made of the equilibrium of the reversible reaction resulting in the formation of the intermediate product, and it was shown that the reaction is exothermic, the heat of reaction being 5.5 kcal/mole.

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SPECTROSCOPIC STUDY OF THE INTERMEDIATE PRODUCT AND INTERMEDIATE STAGE OF REACTION IN THE OXIDATION OF ACETALDEHYDE BY PEROXYACETIC ACID

R. F. Vasilyev, A. N. Terenin, and N. M. Emanuel

Physical methods of investigation have not yet received adequate application in the study of the processes of liquid-phase oxidation by molecular oxygen, and they have not been applied in the study of oxidation by peroxy compounds (i.e. one of the stages in the process of oxidation by molecular oxygen). However, the chemical analysis and identification of individual peroxy compounds taking part in these processes, which have complex mechanisms, comprise a difficult problem that cannot always be solved. There can be no doubt that in this fact lies one of the causes of the inadequate study given to the chemistry of oxidation processes. It is not surprising, therefore, that papers should appear relating to investigations having the object of developing physical methods for the analysis and identification of peroxy compounds, e.g. spectroscopic [1-3] and polarographic [4] methods. It was with this object that systematic studies recently began to be made of various peroxy compounds. Infrared spectra were determined for some dozens of peroxy compounds of various classes [1, 2, 5, 8, 9]. The results obtained were applied in the study of the photochemical [9, 10] and thermal [3] oxidation of aldehydes by molecular oxygen, and in these processes intermediate products - peroxy acids - were detected, and the kinetics of their formation and further transformation were studied.

In the spectra of all of the peroxy compounds absorption bands were found in the frequency range 800-900 cm^{-1}. These bands were ascribed to the valency vibrations of the peroxide linkage $-O-O-$. Theoretically, such an assignment is not well founded, for the vibration at a peroxide linkage is not characteristic [2, 8, 11]. Moreover, other vibrations may also appear in this range (deformational vibrations of the CH_3 group, vibrations of the molecule as a whole, etc.). Actually, it is found that a few bands in the 800-900 cm^{-1} region occur in the spectra of many peroxides.

As these bands are present in the spectra of all peroxy compounds investigated up to the present time, it appears that the presence of an absorption band in the 800-900 cm^{-1} region is a distinguishing feature for peroxy compounds. In the vibration corresponding to this band, not only the $-O-O-$ link takes part, but also neighboring linkages. The position of the absorption band therefore varies (over a range of 100-120 cm^{-1}) according to the structure of the peroxy compound.

We have examined the possibility of applying the spectroscopic method for the study of processes of oxidation by peroxy compounds. As subject for study we selected the oxidation of acetaldehyde by peroxyacetic acid. In so doing we were guided by the following considerations:

a) reaction between aldehydes and peroxy acids is known to be one of the stages in the complex process of the oxidation of aldehydes by molecular oxygen;

b) as a result of work by Soviet and foreign investigators [12-14] it has been established that the reaction selected proceeds stagewise via intermediate formation and subsequent decomposition of an intermediate peroxy compound (Y):

$$CH_3CHO + CH_3COOOH \rightleftharpoons Y \longrightarrow 2CH_3COOH;$$

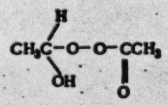
c) the infrared spectra of the original reactants and the final products are comparatively simple and

are well known in the literature.

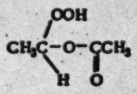
Particular interest was presented by a study of the intermediate stage and intermediate reaction product with the aid of infrared spectroscopy. In its relation to this study, the difference in the position of the −O−O− absorption band in different compounds was regarded by us as a favorable circumstance, since such a difference might insure satisfactory spectroscopic detection of the intermediate peroxy compound in presence of the original peroxy acid. We may point out that the solution of such a problem by chemical methods is often impossible, since the original and intermediate peroxy compound generally have identical chemical properties. Hence, the possibility cannot be excluded that many reactions of this kind that are regarded as simple are in fact processes that proceed in stages.

Kinetic experiments have established that the intermediate peroxy compound is an equimolecular addition product of acetaldehyde and peroxyacetic acid [12-14]. Structural formulas have been proposed in the literature for this compound:

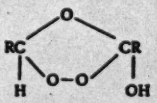
1) 1-Hydroxyethyl peroxyacetate [12]:



2) 1-Hydroperoxyethyl acetate [13]:



3) An isoozonide [15]:



No proof has been advanced for any of these possible structures by the authors who postulated them.

Since the intermediate product is a peroxy compound, it was natural to seek its spectral characteristics in the region of the frequencies of the −O−O− link (800-900 cm^{-1}). As solvent we selected nitromethane, which has a strong but narrow absorption band at 920 cm^{-1} and some other very weak bands in this region. The spectra were determined on an IKS-11 infrared spectrometer having a rock salt prism. The solutions were held in a cell having rock salt windows or in a special cell having polyethylene windows; the latter is the more convenient in work with solutions of such a corrosive substance as peroxyacetic acid. The work was carried out in two stages: preparation of the intermediate product, and the determination of its spectrum. The method of preparing the intermediate product is described in the literature [16]. When toluene solutions of acetaldehyde and peroxyacetic acid are mixed and the mixture is placed in a cryostat, after several hours at −40° to −50° crystals of the intermediate peroxy compound are precipitated (m.p. −19° to −20°). This process is extremely sensitive to variations from optimum concentrations and to impurities (in particular, water). We carried out this preparation, poured the mother liquor from the precipitate, and dried the crystals with the aid of ether. We then dissolved part of the product in nitromethane, filled a cell with the solution, and determined its spectrum. All possible measures were taken to keep the solution at room temperature for as short a time as possible: a portion of the precipitate was dissolved in cooled solvent, the test sample was taken in a cooled pipet, and the time taken to determine the spectrum was confined to a few minutes.

The results are presented in Fig. 1. In the spectrum of the solution of the precipitate powerful absorption is to be clearly observed at a wave number of 847 cm^{-1}, at a place in which the original reactants and final products (acetaldehyde, peroxyacetic acid, and acetic acid) do not have absorption bands. The new

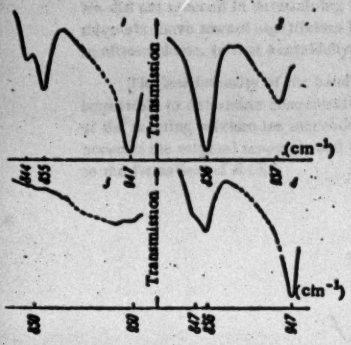


Fig. 1. Spectra of solutions of original reactants, final product, and reacting mixture in the region of the valency vibrations of the −O−O− link: 1) acetaldehyde (0.6 mole/liter); 2) peroxyacetic acid (1.2 moles/liter); 3) acetic acid (1.5 moles/liter); 4) reacting mixture. Thickness of absorbing layer 0.1 mm. Solvent, nitromethane. The broken line indicates the region of the absorption of the solvent.

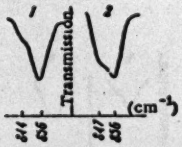


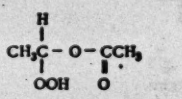
Fig. 2. Summation spectrum of solutions of acetaldehyde and peroxyacetic acid in nitromethane (1), and the spectrum of the reacting mixture (2) (in the region of the valency vibrations of the −O−O− link). Solvent - nitromethane. Thickness of absorbing layer - 0.2 mm. Concentration of solution 0.7 moles/liter.

band partially overlaps the absorption bands of peroxyacetic acid and acetaldehyde (wave number of both of these bands: 856 cm^{-1}) resulting in a characteristic contour having an inflection. When the spectrum is determined on samples that have been kept for 20-30 minutes at room temperature (in the course of this time the intermediate product disappears, being decomposed into acetic acid), the 847 cm^{-1} absorption band is no longer present. This indicates that the new absorption band is definitely not due to foreign substances (such as ether and toluene).

The band of the intermediate product at 847 cm^{-1} was found also in the spectrum obtained when the reaction was carried out directly in nitromethane (without isolation of the crystals). This spectrum is given in Fig. 2. This figure shows also the summation spectrum of aldehyde and peroxy acid solutions. Both spectra were determined in a double cell. Comparison of the spectra shows that the appearance of the 847 cm^{-1} band cannot be explained as the result of the superposition of the bands of the original reactants.

There can be no doubt that the band that we have found at 847 cm^{-1} is an absorption band of the intermediate peroxy compound. It is probably to be attributed to valency vibrations of the −O−O− link. The displacement by 9 cm^{-1} from the spectrum of peroxyacetic acid must be regarded as small when it is considered that the corresponding bands in the spectra of the peroxy compounds that have now been investigated are distributed over a wide range (100-120 cm^{-1}). This result indicates that the change in structure undergone by the molecule does not have a great effect on the dynamics and kinematics of the vibrations of the peroxy link. It may be assumed that this effect will be small when the intermediate product, like peroxyacetic acid, contains a hydroperoxy group, and will not be so small when the hydroperoxy group is converted into peroxy (i.e. to peroxy linked to carbon at both sides) in the course of the reaction *.

In view of the spectroscopic results therefore, of the three structures proposed in the literature for the intermediate compound the most probable is that postulated by Bawn and Williamson - 1-hydroperoxyethyl acetate:



* Data in the literature give convincing support to this view. Karyakin and Nikitin [1] observed only small displacements of bands in the region 800-900 cm^{-1} in a series of cyclic hydroperoxides, but could not distinguish bands that preserved their position in a series of peroxides. According to Minkov's results [2] on the spectra of about thirty peroxides and hydroperoxides, the most intensive bands are distributed as follows: in the spectra of peroxides - in the range 820-890 cm^{-1}; in the spectra of hydroperoxides - in the much narrower range 835-855 cm^{-1}.

We did not succeed in determining the band of the intermediate product in the isolated state, since a considerable move toward equilibrium between it and the original reactants always occurred during its dissolution in nitromethane, so that acetaldehyde and peroxyacetic acid were always present in the solution.

The low intensity of the band and the overlapping of this band and that of peroxyacetic acid made it impossible to determine concentrations quantitatively by spectrum analysis. Nevertheless, from the spectrum of the reacting mixture we succeeded in following qualitatively the kinetics of the establishment of equilibrium between the original reactants and the intermediate peroxy compound and the kinetics of the reaction leading to the formation of acid.

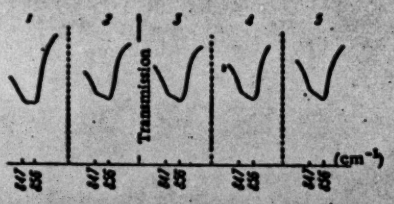


Fig. 3. Spectra of reacting mixture: 1) immediately after dissolution of crystals in nitromethane; 2) 11 minutes after dissolution; 3) after 23 minutes; 4) after 68 minutes; 5) after 73 minutes. Thickness of absorbing layer - 0.1 mm. Temperature - -10°.

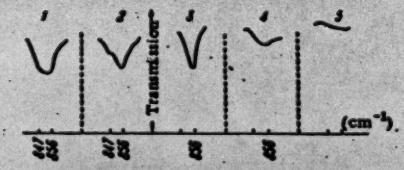


Fig. 4. Spectra of reacting mixture: 1) immediately after dissolution of intermediate product; 2) 9 minutes after dissolution; 3) after 22 minutes; 4) after 50 minutes; 5) after 80 minutes. Thickness of absorbing layer - 0.1 mm. Temperature - +20°.

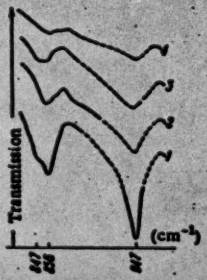


Fig. 5. Spectra of reacting mixture: 1) immediately after dissolution of intermediate product; 2) after 21 minutes; 3) after 41 minutes; 4) after 54 minutes. Room temperature.

Figures 3 and 4 give the results of two experiments, carried out at −10° and +20° respectively. In both experiments the intermediate product, which separated in the form of crystals, was dissolved in nitromethane. The resulting solution was placed in a thermostat (−10° or +20°), test samples were transferred to the cell, and the spectrum was recorded.

In experiments on the kinetics of the oxidation of acetaldehyde by peroxyacetic acid [14] it was established that the temperature coefficients for the reactions of formation of the intermediate product and its decomposition into the original reactants are less than the temperature coefficient for the reaction of formation

of acetic acid. For this reason, scarcely any acetic acid is formed at −10°, and reaction consists only in the establishment of equilibrium between the original reactants and the intermediate peroxy compound. Accordingly, the intensity of the band of the intermediate product (847 cm^{-1}) diminishes relative to that of the peroxyacetic acid band (856 cm^{-1}) and finally takes up a constant value (Fig. 3). At 20° establishment of equilibrium and decomposition of the intermediate product into acid proceed simultaneously, the first process being the more rapid so that the intensity of the band due to the intermediate product diminishes at first, and then also that due to peroxyacetic acid diminishes (Fig. 4).

Fig. 5 shows a series of spectrograms taken in succession over a wider range of frequencies. The solution from which the test samples were taken was at room temperature. The gradual disappearance of the absorption bands of peroxyacetic acid (856 cm^{-1}), the intermediate product (847 cm^{-1}), and acetaldehyde (847 cm^{-1}) can be clearly seen.

SUMMARY

1. The intermediate product formed in the oxidation of acetaldehyde by peroxyacetic acid was isolated in the form of crystals. A band at 847 cm^{-1} was found in the absorption spectrum of its solution, and this was ascribed to the vibration of the peroxy link in the molecule of the intermediate product.

2. The variation of the spectrum of the reacting mixture with time is in full accord with a stagewise reaction mechanism. The presence of an intermediate stage and an intermediate product is quite clearly manifest in the spectrum - a fact that indicates that the application of infrared spectroscopy to the study of oxidation by peroxy compounds forms a promising line of attack on this problem.

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EFFECT OF SOLVENTS ON THE RATE OF OXIDATION OF ACETALDEHYDE BY PEROXYACETIC ACID FROM THE POINT OF VIEW OF INTERMOLECULAR HYDROGEN BONDING

R. F. Vasil'yev, A. N. Terenin, and N. M. Emanuel

Whenever a study is made of the kinetics of a reaction in solution, the question of the effect of the solvent on the rate and mechanism of the process is bound to arise. It then becomes important to determine how the observed effect of the solvent arises.

We have carried out experiments on the kinetics of the oxidation of acetaldehyde by peroxyacetic acid in eight different solvents: carbon tetrachloride, chloroform, toluene, benzene, nitrobenzene, methanol, nitromethane, and acetone. The reaction between peroxyacetic acid and acetaldehyde results in the formation of acetic acid, and it occurs in stages via the reversible formation and subsequent decomposition of an intermediate peroxy compound Y [1]:

$$CH_3COOOH + CH_3CHO \rightleftharpoons Y \longrightarrow 2CH_3COOH.$$

With the object of obtaining reproducible results, we adopted the procedure of diluting stock solutions with solvents. As stock solutions we prepared solutions of peroxyacetic acid and acetaldehyde in toluene. At the beginning of an experiment 1.5 ml of the aldehyde stock solution was diluted with 10 ml of solvent, and 0.5 ml of peroxy acid stock solution was then mixed in. Hence, all of the experiments were carried out with the same solutions, and the solvent whose effect was being studied comprised about 84% of the volume of the reacting mixture. This procedure made it possible to compare quantitatively the rates of the process in various solvents. Kinetic measurements were made for diminution in the amounts of peroxyacetic acid and in total active oxygen, i.e. the active oxygen present both as peroxyacetic acid and as intermediate product. Stoichiometric considerations show that the latter kinetic relationship is identical with the kinetics of acetic acid formation.

The experimental results are shown in Fig. 1, from which it will be seen that the rate at which peroxyacetic acid is used up is identical in chloroform, toluene, benzene, and nitrobenzene; the rate is somewhat higher in carbon tetrachloride. In all of these solvents the formation of the intermediate peroxy compound proceeds to approximately the same degree of transformation, namely 70-78%. The rate at which the intermediate peroxy compound is formed in methanol, nitromethane, and acetone* is very much less than in the solvents of the first group.

In all of the solvents the two stages of the reaction are clearly marked. The solvents vary in their effects on the rates of the two stages. For example, the intermediate product is formed more slowly in methanol than in solvents of the first group, whereas the rate of the decomposition of the intermediate product into acid is higher in methanol than in any of the other solvents.

Our experimental results on the dependence of the course of the reaction on the identity of the solvent

* Special experiments showed that acetone is not oxidized by peroxyacetic acid at 24.2°.

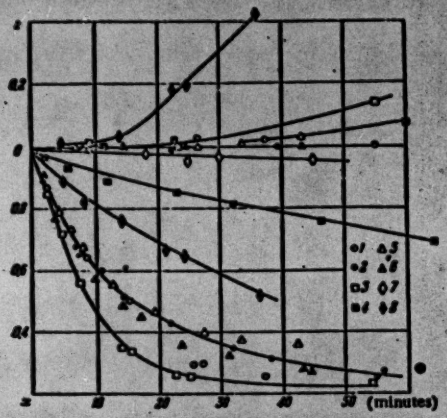


Fig. 1. Kinetics of the consumption of peroxyacetic acid (x) and the formation of acid (z) in various solvents at 24.2°: 1) in carbon tetrachloride; 2) in chloroform; 3) in toluene; 4) in benzene; 5) in nitrobenzene; 6) in methanol; 7) in nitromethane; 8) in acetone. Initial concentrations: peroxyacetic acid 0.273 mole/liter; acetaldehyde 0.216 mole/liter.

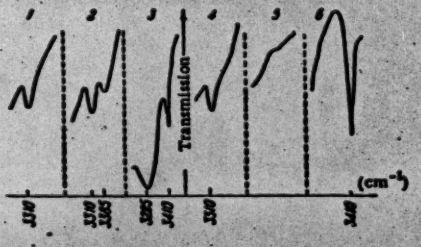


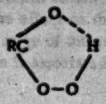
Fig. 2. Infrared spectra of peroxyacetic acid solutions (0.7 mole/liter): 1) in toluene; 2) in 1:1 mixture of toluene and nitromethane; 3) in 1:1 mixture of toluene and acetone; 4) in 1:1 mixture of toluene and nitrobenzene; 5) spectrum of pure nitromethane; 6) spectrum of pure acetone. Thickness of layer - 0.1 mm.

can be interpreted as follows. The molecular structure of the solvents in which the first stage of reaction is slow (methanol, acetone, nitromethane) is such that hydrogen bonding is possible between the solvent molecule and the molecule of peroxyacetic acid. A hydrogen bond can be formed between the hydroxyl group of the peroxy acid on the one hand and the hydroxyl, carbonyl, or nitro group of the solvent on the other. The possibility of the formation of a second hydrogen bond cannot be excluded, i.e. between the carbonyl group of the per-

oxy acid and the hydroxyl groups of the solvents. For the remaining solvents (with the exception of nitrobenzene) we may state before hand that the formation of such hydrogen bridges is impossible on account of the absence of suitable structural groups.

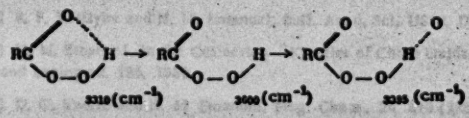
The presence of solvent molecules linked to reactant molecules by hydrogen bonds can affect reaction rate. The kinetic detection of a hydrogen bond was considered in investigations by one of us and coworkers [2, 3]. In these investigations it was established that in certain cases hydrogen bonding has a great effect on the kinetics of chemical reactions. In particular, it was found that it was possible to detect intermolecular hydrogen bonding by kinetic methods [4]. In our case, solvent molecules hydrogen-bonded to peroxyacetic acid molecules can reduce the accessibility of the latter to acetaldehyde molecules and so bring about a reduction in reaction rate.

As is well known, the most reliable method for establishing the presence of a hydrogen bond consists in a study of the vibration spectra (infrared and Raman) of suitable mixtures [5]. Hydrogen bonding causes a displacement and broadening in the bands of the links concerned in the hydrogen-bond formation. For example, the wave number of the vibrations of a hydroxyl in any compound is 3600-3750 cm^{-1}, which is reduced when the hydroxyl is hydrogen-bonded to 3000-3500 cm^{-1}, depending on the strength of the hydrogen bond. We studied the infrared absorption spectra of peroxyacetic acid solutions in the range 3000-3500 cm^{-1}. The infrared spectra were recorded with an IKS-11 infrared spectrometer having a lithium fluoride prism. The solvents used were equimolecular mixtures of toluene with nitromethane, nitrobenzene, and acetone. The spectrum of a solution of the peroxy acid in methanol was not determined because the solvent itself absorbs strongly in this region of the spectrum owing to association due to hydrogen bonding. The spectra obtained are given in Fig. 2. In toluene solution in this region of the spectrum there is an absorption band at 3310 cm^{-1}, which must be attributed to an intramolecular hydrogen bond formed in molecules of aliphatic peroxy acids [6, 7]:



(the wave number of the "free", i.e. not hydrogen-bonded, hydroxyl is in this case 3600 cm^{-1}).

When nitromethane is added to a toluene solution of peroxyacetic acid, a new band (3385 cm^{-1}) appears which is present neither in the toluene spectrum nor in the nitromethane spectrum. We attribute this band to the vibrations of the hydroxyl group of the peroxy acid, which is hydrogen-bonded to the nitromethane molecule. We consider that in some of the peroxy acid molecules the intramolecular hydrogen bond is broken and the "freed" hydroxyl group attaches itself to an oxygen atom of nitromethane:



When acetone is added to a toluene solution of peroxyacetic acid, considerable changes occur in the spectrum: the band broadens and increases in intensity, and its maximum is displaced toward the long waves, and takes up the position 3265 cm^{-1}. Since pure acetone does not absorb in this region it is natural to assume that the new absorption band is associated with a hydrogen bond between the acetone and peroxyacetic acid molecules:

The high intensity of the band - higher than in nitromethane solution - indicates that a larger number of molecules are hydrogen-bonded. It is possible that it is for this reason that the rate of reaction in acetone is lower than in the other solvents. The addition of nitrobenzene does not affect the spectrum of a solution in toluene, a fact that indicates that no hydrogen bonding occurs between nitrobenzene and peroxyacetic acid. It is known that nitrobenzene, owing to its low basicity, does not form a strong hydrogen bond [8]. It should be noted that in nitrobenzene reaction proceeds at the same rate as in chloroform, toluene, and benzene, i.e., in the solvents that cannot be hydrogen-bonded to peroxyacetic acid on account of the absence of suitable structural groups. There can be no doubt that a hydrogen bond is formed between methanol and peroxyacetic acid, although we were unable to establish this directly.

Practically no work has been reported in the literature on the effect of solvents on the rate of oxidation by peroxy acids. Such data as exists, however, confirm our hypothesis concerning the effect of the hydrogen bond on the reaction. Meerwein and Bodendorf [9] studied the oxidation of propenylbenzene and anisaldehyde by peroxybenzoic acid. It was found that the rates of these two reactions were considerably lower in ether, acetone, and ethanol than in nitrobenzene, chloroform, benzene, carbon tetrachloride, and cyclohexane. It will be seen that, in this case also, reaction is slower in solvents that form hydrogen bonds than in those that are unable to form hydrogen bonds. Jorrisen and van der Beek [10, 11] found that only in an acetone solvent could they succeed in isolating peroxybenzoic acid formed by the autoxidation of benzaldehyde; in other solvents it disappeared instantaneously owing to rapid reaction with benzaldehyde. According to Kagan and Lyubarsky [12], the rate of the oxidation of acetaldehyde by peroxyacetic acid is almost the same in benzene, chloroform, nitrobenzene, and toluene (i.e., in the solvents that do not form hydrogen bonds with peroxyacetic acid).

Thus, on the basis of the results obtained by us and by other workers we may conclude that the presence of a hydrogen bond has a definite effect on the rate of oxidation of acetaldehyde by peroxyacetic acid (more exactly, on the rate of the first stage of this reaction). This explains the difference in the kinetics in different solvents: retardation of reaction is associated with the blocking effect of solvent molecules hydrogen-bonded to peroxyacetic acid molecules.

SUMMARY

It was shown that retardation of reaction found in some solvents is due to the blocking effect of solvent molecules hydrogen-bonded to peroxyacetic acid molecules. The presence of hydrogen bonds between peroxyacetic acid molecules and solvent molecules (nitromethane, acetone) was established by the determination of infrared absorption spectra.

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KINETIC METHOD OF APPLYING LABELED ATOMS IN THE INVESTIGATION OF COMPLEX CHEMICAL AND BIOCHEMICAL PROCESSES

COMMUNICATION 6. RATES OF FORMATION AND TRANSFORMATION OF ACETALDEHYDE, CARBON MONOXIDE, AND CARBON DIOXIDE IN THE OXIDATION OF PROPENE

M. B. Neiman, V. Ya. Efremov, N. K. Serdyuk, and A. F. Lukovnikov

In spite of the large number of investigations that have been devoted to the oxidation of hydrocarbons, the mechanism of this complex process has not yet been adequately studied. No unified view has been established even with respect to the basic features of the mechanism. Thus, some authors consider that the substance causing degenerate branchings is a peroxy compound, and others that it is acetaldehyde. Some authors consider that acetaldehyde is simultaneously formed and consumed in the course of the reaction [1], and others consider that the consumption of acetaldehyde comes practically to a stop in the period when rapid oxidation of the hydrocarbon is occurring [2]. The question of the ways in which carbon oxides are formed and their rates of formation is also obscure. All of these questions have been investigated previously mainly by classical methods. As we considered that the kinetic method that we have developed could give some help in the elucidation of these matters, we have now investigated the oxidation of propene by this method.

As we were interested primarily in the behavior of acetaldehyde, we decided to carry out experiments on oxidation in a propene - oxygen mixture to which a small amount of $CH_3C^{14}HO$ was added. Some series of experiments were also carried out with additions of $C^{14}O$.

So that the kinetic method could be applied it was necessary first to develop a procedure for the determination of the acetaldehyde concentration in the oxidation products of propene, in which it was possible that some other aldehydes might be present. Also, it was necessary to determine whether hydrogen could be transferred from alcohols to acetaldehyde in accordance with the equation:

$$CH_3C^{14}HO + RCH_2OH \rightleftharpoons CH_3C^{14}H_2OH + RCHO.$$

It will be seen that transfer of hydrogen atoms between alcohol and aldehyde could result in the formation of labeled alcohol from labeled aldehyde, which, if the kinetic method were applied, would distort the results of radiochemical analysis.

EXPERIMENTAL

Synthesis of Reactants. Experimental Conditions. Propene was prepared by dehydration of isopropyl alcohol over a catalyst. It was carefully purified. Mass-spectrometric analysis showed that our product did not contain more than 0.3% of butenes.

Labeled carbon monoxide was prepared by catalytic exchange in the reaction:

$$CO + C^{14}O_2 \rightleftharpoons C^{14}O + CO_2$$

as described in the paper [3].

Acetaldehyde labeled with radioactive carbon in the carbonyl group was prepared as follows:

$$CH_3C^{14}OOH \xrightarrow[H_2SO_4]{C_2H_5OH} CH_3C^{14}OOC_2H_5 \xrightarrow{LiAlH_4} CH_3C^{14}H_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3C^{14}HO,$$

as described in the paper [4].

The experiments on the oxidation of propene were carried out in a glass vacuum apparatus. The volume of the reaction vessel was 205 ml, and its diameter was 4 cm.

For the investigation by the kinetic method we isolated carbon oxides and acetaldehyde from the oxidation products. The concentrations and specific activities of these products were determined by methods described previously [3, 5].

Determination of the Acetaldehyde Content. In order to apply the kinetic method it was necessary to know the acetaldehyde concentration, not the total concentration of aldehydes. Since the higher aldehydes are reduced at the same potential as acetaldehyde, it was necessary to establish whether the reaction products included any higher aldehydes and whether other oxygen-containing products present affected the height of the polarographic wave for acetaldehyde.

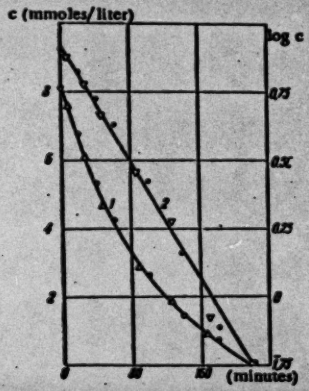

Fig. 1. Concentration of a standard acetaldehyde solution (o) and of a solution of the oxidation products of propene (v) as a function of the duration of passage of hydrogen (Curve 1); the same curve plotted in the coordinates log c and time (Curve 2)

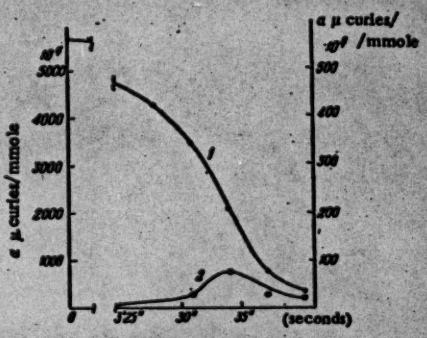

Fig. 2. Variation in specific activity: 1 - CO_2; 2 - CO_2

It has been established previously that, when hydrogen is blown through an aqueous solution of a volatile compound, the concentration of the latter varies according to the law

$$x = x_0 e^{-kt} \qquad (1)$$

in which x is the concentration of the substance being blown out, x_0 is its initial concentration, t is the duration of blowing, and k is a constant. To a fairly close approximation, the constant k can be calculated from the formula:

$$k = \frac{Ap_0\alpha}{1244V}, \qquad (2)$$

in which A is the rate of blowing, p_0 is the vapor pressure of the substance investigated, V is the volume of the solution, and α is a coefficient characterizing the departure of the given solution from the ideal.

The value of k can be found also experimentally from the curve for the dependence of the concentration of the volatile compound on the duration of blowing with hydrogen. If we plot $x = f(t)$ [1] in the coordinates log x and t, k will be equal to the slope of the curve. For a complex mixture of compounds having various vapor pressures, the slope of the curve will vary and the value of k will be different.

It appeared to us, therefore, to be possible to decide whether any higher aldehydes were present in the mixture by comparison of the curves for the variation in concentration during the passage of hydrogen through a solution of pure acetaldehyde and through an actual mixture of the oxidation products of propene. Hydrogen was passed through an electrolytic vessel containing the solution of acetaldehyde or reaction products at a rate of 10.5 ml/minute at 22°. After a period of 20-60 minutes, blowing was discontinued and polarography was carried out in 0.1 N LiCl. The results of the experiments are presented in Fig. 1. The points corresponding to the acetaldehyde concentration in the solution of reaction products and in the standard acetaldehyde solution lie on a single curve. The coincidence of the curves indicates that higher aldehydes are substantially absent from the reaction products, and other oxygen-containing compounds do not affect the height of the polarographic wave for acetaldehyde. The same conclusion follows from a comparison of the values of the constant k calculated from Equation 2* and found from the slope of the straight line $\log x = f(t)$.

Study of the Possibility of Hydrogen Transfer in a Mixture of Alcohol and Acetaldehyde. In order to resolve this matter, an equimolecular mixture of CH_3CHO and $CH_3C^{14}H_2OH$ was heated in a glass vessel for several hours. The acetaldehyde was then analyzed radiochemically. Over the temperature range studied (315-387°) we did not detect any appreciable transfer of hydrogen from alcohol to acetaldehyde. The specific activity of acetaldehyde was about 3 conventional units irrespective of the duration of heating (the original specific activity of the alcohol was 500 units). It is possible that there was a slight amount of oxygen in the original mixture of alcohol and acetaldehyde, and this immediately oxidized $CH_3C^{14}H_2OH$ to $CH_3C^{14}HO$ and was then used up. When the mixture was heated further, the specific activity of the acetaldehyde did not change. In view of the minute extent, or even absence, of hydrogen transfer, we may neglect it.

Experimental Results

Oxidation of Propene in presence of $C^{14}O$ and CO_2. In order to establish the course of the process of CO_2 formation in the oxidation of propene and the proportion of it that is formed from CO, we carried out experiments on the oxidation of propene containing additions of $C^{14}O$ and CO_2. Oxidation was carried out in a mixture of 48% of C_3H_6, 50.7% of O_2, 1.08% of CO_2, and 0.22% of $C^{14}O$ at 340° and an initial pressure of 281 mm. The variation in the specific activities of CO and CO_2 in the course of the process is shown in Fig. 2. As can be seen from Fig. 2, the specific activity of carbon monoxide falls fairly rapidly, whereas that of carbon dioxide rises at first, passes through a maximum, and then falls off. If CO_2 were formed solely from CO, then at the maximum the specific activity curve for CO_2 would intersect the specific activity curve for CO. In our case the maximum α_{CO_2} lies considerably below the α_{CO} curve. This indicates that CO_2 is formed partially from CO, but mainly from other reaction products.

According to the equations for the kinetic method [3], the specific activities of CO and CO_2 and the rates of formation of CO_2 by parallel routes are related together at the point corresponding to maximum α_{CO_2}

* The value of $p_0\alpha$ was found from $p = p_0 x\alpha$, in which p is the partial vapor pressure of acetaldehyde in aqueous solution and x is its concentration. The dependence of p on x for acetaldehyde has been studied by Dobrinsky [7].

by the equation

$$\frac{w}{w_1} = \frac{a_{CO}}{a_{CO_2}}, \qquad (3)$$

in which w_1 is the rate of formation of CO_2 from carbon monoxide, and w is the overall rate of formation of CO_2 (by all routes).

It follows from our results that

$$\frac{a_{CO}}{a_{CO_2}} = 26.$$

This means that only 3-4% of carbon dioxide is formed by the oxidation of carbon monoxide. The bulk of it is formed in other ways.

These results are in accord with those obtained in an investigation of the behavior of CO and CO_2 in the butane oxidation [3], so that we may infer that there is a general mechanism for the formation of CO_2 which is common to the oxidation of saturated and unsaturated hydrocarbons.

Oxidation of Propene in presence of $CH_3C^{14}HO$. Experiments on the oxidation of propene in presence of $CH_3C^{14}HO$ was carried out with the mixture of 50% of O_2, 48.87% of C_3H_6, and 1.13% of $CH_3C^{14}HO$, the initial pressure being 243 mm and the temperature 315°. The kinetic curve, characterized by the occurrence of four cool flames, is shown in Fig. 3.

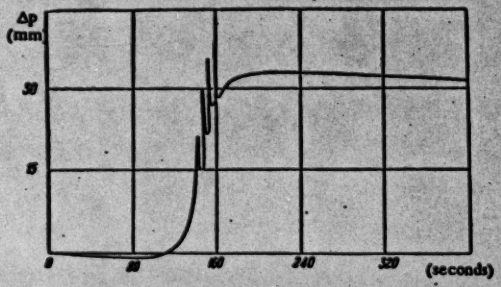

Fig. 3. Variation in pressure during the oxidation of propene (p_0 243 mm; temperature 315°)

The curves for the variation in concentration and specific activity of acetaldehyde are presented in Fig. 4. It should be noted that the fall in the specific activity of acetaldehyde with time does not correspond to the rise in its concentration; the latter changes much more rapidly than the former. Thus, before the cool flames occur, the concentration has grown by a factor of 3.8, whereas the specific activity has fallen by a factor of 5.5. After the extinction of the cool flames, the concentration increases by a factor of 5.5 and the specific activity falls by a factor of 19.5. This indicates that acetaldehyde is being consumed as well as formed.

Discussion of Experimental Results

From a knowledge of the way in which the concentration and specific activity of acetaldehyde vary, we may calculate the rates at which it is formed and consumed. It is known [8] that

$$-\frac{da}{dt} = \frac{aw}{x}, \qquad (4)$$

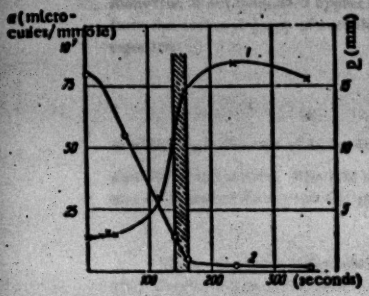

Fig. 4. Variation in concentration (Curve 1) and specific activity (Curve 2) of acetaldehyde (the shaded area corresponds to the cool-flame zone)

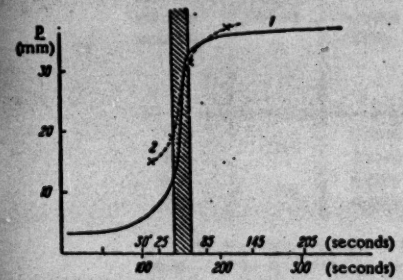

Fig. 5. Kinetics of the formation of acetaldehyde, no account being taken of its subsequent consumption (Curve 1). Curve 2 is constructed from Polyak and Shtern's data

in which α is the specific activity of acetaldehyde, w is the rate of its formation, and x is its concentration,

The amount of acetaldehyde formed at rate w in time t, its further oxidation not being taken into account, is

$$c = \int_0^t w\,dt. \qquad (5)$$

Substituting the value of w from Equations 4 and 5, we obtain

$$c = \int_{\alpha}^{\alpha_0} x\,d\ln\alpha. \qquad (6)$$

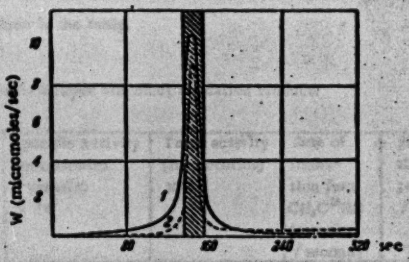

Fig. 6. Rates of formation (Curve 1) and consumption (Curve 2) of acetaldehyde in the cool-flame oxidation of propene

Having constructed the curve $x = f(\ln \alpha)$, we find c by graphical integration. The kinetics of the formation of acetaldehyde - its further oxidation not being taken into account - is shown in Fig. 5. In this figure we give also the analogous curve obtained by Polyak and Shtern [9] in work on the cool-flame oxidation of propene under identical conditions. A comparison of the courses of the curves shows that, when the cool-flame zone is passed, Polyak's results are almost identical with ours. As regards the period of induction, there are serious discrepancies. It is probable that substantial corrections must be made in the method of calculation used by these authors.

Knowing the actual kinetics of the accumulation of acetaldehyde, we may determine its rate of formation by graphical differentiation of the curve $c = f(t)$ (Fig. 5). The difference between the rates of formation and accumulation (the latter is found by graphical differentiation of Curve 1, Fig. 4) gives the rate of consumption. The rates so calculated are represented in Fig. 6, from which it will be seen that both formation and consumption occur throughout the whole course of the oxidation as far as the extinction of the cool flames. After the extinction of the cool flames the rate of formation of acetaldehyde falls almost to nil, although the rate of its consumption still remains appreciable.

Our conclusions are in conflict with those of Feklisov and Neiman [2] in their work on the behavior of acetaldehyde in the oxidation of butane.

Taking into account the fact that carbon dioxide is an end product of the oxidation and that carbon monoxide is not converted appreciably into dioxide, we calculated the rate of formation of these compounds from the carbonyl group of acetaldehyde and from other products. The rate of formation is found from the equation

$$w_1 = \frac{1}{\alpha_{CH_3CHO}} \frac{dI}{dt}, \qquad (7)$$

in which w_1 is the rate of formation of CO or CO_2 from acetaldehyde and $\frac{dI}{dt}$ is the rate of change of total activity of CO or CO_2. The rate of formation of CO and CO_2 by other routes (w_2) is the difference between the rate of accumulation w and the rate of formation from acetaldehyde:

$$w_2 = w - w_1. \qquad (8)$$

These rates were calculated from data obtained by analysis of the products before the formation of and after the extinction of the cool flames.

The results of the calculation are given in the table.

TABLE

Rates of Formation of CO and CO_2 from Acetaldehyde and other Oxidation Products

Duration of reaction (seconds)	Reaction product	Concentration (mmoles / liter)	Specific activity (microcuries / mmole) x 10^7	Total activity (microcurics) x 10^6	Rate of formation from $CH_3C^{14}HO$ (mmole / second)	Rate of formation from other products (mmole / second)
140	CO	0.1006	2.31	2.3	0.0041	0.013
160		0.4380	2.27	9.7		
140	CO_2	0.0394	15.7	6.2	0.002	0.002
160		0.1210	7.9	9.8		

The table shows that the rate of formation of CO from acetaldehyde in the cool-flame zone is only one-third of the rate of its formation by other routes. Carbon dioxide is formed from acetaldehyde and from other products at approximately equal rates. It follows from these considerations that, in the cool-flame zone, about one-half of the CO_2 and about 30% of the CO are formed from the carbonyl group of the acetaldehyde.

SUMMARY

1. It was shown by the blowing method that acetaldehyde can be determined polarographically in the products of the oxidation of propene.

2. It was shown that, at temperatures up to 387°, no hydrogen transfer occurs in alcohol-acetaldehyde mixtures.

3. It was shown that most of the carbon dioxide produced in the oxidation of propene is not formed by the oxidation of carbon monoxide.

4. It was shown that, in the oxidation of propene, acetaldehyde is formed and consumed at comparable rates.

5. It was shown that, in the cool-flame zone, about 50% of the carbon dioxide and 30% of the carbon monoxide are formed from the carbonyl group of acetaldehyde.

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* T.p. = C. B. Translation pagination.

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CRITERIA FOR CHAIN REACTIONS

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The main features distinguishing chain and radical processes from molecular processes are considered to be certain kinetic peculiarities, marked critical phenomena (in branched chain reactions), anomalously high quantum yields (in photochemical chain processes), appreciable acceleration or retardation when small additions are made, fundamental changes in kinetics when free radicals are added to the reacting system, etc. [1]. It must be noted that these criteria enable us to make a choice between chain, radical, and molecular mechanisms only when the relevant experiments give positive results. If, however, one or more chan- ne listed characteristics are absent, then it is generally not possible to affirm on this basis that a process is definitely a molecular one. It is often not less difficult to establish whether a reaction in which radicals take part is a chain reaction or simply a radical reaction.

An approach may be made to the solution of problems relating to the mechanism of a complex reaction on the basis of an analysis of the general problem of the concentrations of free radicals in the course of a chemical transformation. In fact, an examination of the usual chain reaction schemes - both for branched and for unbranched processes - leads to the conclusion that the high rates of such processes are associated with the formation, in the course of the reaction, of higher than equilibrium concentrations of free radicals (with respect to equilibrium with the original reactants). In purely radical thermal reactions, the concentrations of free radicals are always less than the equilibrium concentrations. On the other hand, in molecular reactions, in which the final products are formed without the participation of radicals, the concentrations of the latter always correspond to equilibrium with the original molecules.

It follows from these considerations that the most direct method of determining the character of a chemical process would be the exact measurement, in the given system, of the concentrations of those radicals which could result in the formation of the final products, and comparison of the values obtained with equilibrium values. Our experimental methods, however, permit us to measure absolute concentrations of radicals only in systems in which [R] attains a value of at least some hundredths of a millimeter (for example [H] and [OH] in rarefied flames of hydrogen and carbon monoxide [2]). When the value of [R] is appreciably less than this, as in such processes as the oxidation of hydrocarbons and unbranched chain reactions of halogenation, polymerization, thermal decomposition, etc., the direct does not appear to be possible. The exact determination of this ratio is rendered difficult also by the fact that absolute values of $[R]_{equil}$ can be calculated only very approximately for radicals that are at all complex: thermodynamic functions for such radicals are unknown, and the experimental determination of $[R]_{equil}$ is in most cases practically impossible. In spite of these difficulties, a choice between chain, radical, and molecular mechanisms may sometimes be made for processes which can be carried out reversibly under the conditions in which we are interested.

At the basis of the proposed method for the identification of the mechanism lies a quite obvious postulate, namely, that in an equilibrium system, the concentration of free radicals has its equilibrium value with respect to any of the reacting substances. Let us examine two reaction systems. In system (1) the reaction

$$A_1 + A_2 + \ldots \rightarrow B_1 + B_2 + \ldots \qquad (1)$$

proceeds with given concentrations of the starting substances (A_1), (A_2)... under given conditions. In system

(2), under the same external conditions, to the original substances at the initial concentrations (A_1), (A_2), etc., the final products are added in concentrations exactly corresponding to equilibrium conditions. It is quite obvious that no chemical reaction will be observed in system (2); for example, the concentration of A_1 will not change with time. However, since chemical equilibrium has a dynamic character, in such an equilibrium system two opposed processes - the consumption and formation of A_1 - will be constantly proceeding at equal rates.

Let us compare the concentrations of like radicals (or the total concentrations of radicals) in the two systems for different assumptions regarding the mechanism of the process. If it is a molecular reaction, then for any of the radicals:

$$[R_i]_I = [R_i]_{II} \quad \text{and} \quad (\Sigma_i[R_i])_I = (\Sigma_i[R_i])_{II}.$$

If it is a radical reaction, then at least for one of the radicals of the system,

$$[R_i]_I < [R_i]_{II} \quad \text{and} \quad (\Sigma_i[R_i])_I < (\Sigma_i[R_i])_{II}.$$

If it is a chain reaction, then at least for one radical, and sometimes for all,

$$[R_i]_I > [R_i]_{II} \quad \text{and} \quad (\Sigma_i[R_i])_I > (\Sigma_i[R_i])_{II}.$$

Hence, in order to establish the main features of the mechanism, there is no need to measure the absolute concentrations of free radicals. For this purpose it is quite sufficient to determine relative concentrations, and as a standard for comparison it is most convenient to select concentrations observed when the process is carried out under equilibrium conditions.

For the determination of relative concentrations of radicals, spectrum, magnetic-resonance, and mass-spectrometric methods can be used. We consider that in this way the question of the mechanism of the process - understood in the sense already indicated - can be solved unequivocally (only for reversible processes, of course).

Another approach to the solution of the question under consideration can be made by chemical methods; in particular, by the method of labeled atoms. Since the concentration of free radicals (in the case of chain and radical reactions) is unequivocally associated with the rate of the process, a comparison of the rate of reaction (1) in system I (w_I) with the rate of the transformation of the original reactants in the same direction in system II (w_{II}) should enable us to distinguish between the mechanisms in which we are interested. The greatest difficulty lies in the discovery of a method for the separate determination of the forward and reverse reactions in reversible processes. The only method available at present for the solution of this problem is the method of labeled atoms. If we label the molecules of one of the components of the original mixture (e.g. A_1), then by the rate at which A^*_1 is consumed (or the rate at which B^*_1 is formed) we may form an idea of the rate of the forward reaction in the equilibrium system II in a number of cases. We consider that this method may enable us to make a very clear distinction between chain reactions on the one hand and radical and molecular reactions on the other.

In the case of molecular processes the reaction rate depends, by definition, only on the concentrations of the original substances, and, since these concentrations are the same in both systems,

$$w_I = w_{II}.$$

in which w_{II} is the rate of reaction in system II measured with the aid of labeled atoms.

If the reaction (1) proceeds by a chain mechanism, then the rate at which the substance A is consumed can be written

$$-\frac{d[A_1]}{dt} = k[R_i][A_1].$$

in which k is the rate constant for the elementary process of interaction between the molecule A and the corresponding radical of the system (in this case R_1). Since in the equilibrium system II $[R_i]$ is less than in

system I,

$$w_I > w_{II}$$

In radical mechanisms $[R_i]$ is greater than $[R_i]_I$, and it would be expected that w_{II} would be greater than w_I.

This relationship holds, however, only in radical processes in which the molecule containing the labeled atom does not dissociate into radicals. For example, if we assume that the iodination of hydrogen has the radical mechanism recently proposed by Semenov [3]:

$$\left.\begin{aligned} M + I_2 &\underset{k_b}{\overset{k_a}{\rightleftarrows}} 2I + M \\ 2I + H_2 &\xrightarrow{k_c} 2HI \end{aligned}\right\} \quad (X)$$

and use deuterium or tritium as a labeled molecule, then it can be shown that the rate of consumption of H_2 under equilibrium conditions should be $(1 + k_c[H_2]/k_b[M])$ times as great as that obtaining when reaction is carried out in absence of HI. Such experiments might enable us to make a choice between the scheme given above and a molecular mechanism.

However, in radical reactions in which the labeled molecule takes part in the formation of radicals, for example:

$$A_1 + A_2 + \cdots \underset{k_b}{\overset{k_a}{\rightleftarrows}} R_1 + R_2 + \cdots \rightleftarrows B_1 + B_2 \cdots .$$

the rates w_I and w_{II} are found to be equal. This is explained by the fact that in such processes the values of w_I and w_{II} are not, strictly speaking, the rates of consumption of the original molecules, but are only differences between the rates of two reversible processes (a) and (b). Taking this circumstance into account, for radical reactions in general we find that

$$w_I \leq w_{II}.$$

The method of labeled atoms, therefore, is somewhat less versatile for the solution of our problem than any of the methods of determining relative concentrations of free radicals. It is, however, quite applicable as a criterion for chain mechanisms, which is a matter of great significance at the present time [3].

There are no data in the literature relating to the comparison of w_I and w_{II} in radical, chain, and molecular reactions. Similar considerations can be applied also in the analysis of data on the course of ionic and heterogeneous processes. In this connection we may mention the work of Wilson and Dickenson [4], in which data on the determination of w_{II} for the oxidation of arsenious acid labeled with radioactive arsenic to arsenic acid in presence of iodide ions were compared with the results of Roebuck and others [5], who studied the same reaction under conditions far removed from equilibrium. As direct exchange between the two acids did not occur under the conditions of these experiments - as was shown by special experiments - the authors' suggestion that the process proceeds by a dissociation-association ionic mechanism appears very probable. The reaction scheme proposed by Roebuck and others on the basis of kinetic data is based on the hypothesis that the determining stage is the reaction of the iodide ion (in the form I_3^-) with the undissociated arsenious acid molecule. Such a mechanism is quite analogous from the kinetic point of view to the radical mechanism discussed above. From our discussion it follows that in this case the rate of exchange in the equilibrium system (w_{II}) may be somewhat higher than the rate in a system in which the final product is absent (w_I). The numerical values of the effective constants given in the paper [4] are, respectively, 0.071 and 0.057 at 25° and 0.154 and 0.125 at 35°. It may therefore be considered that comparison of the values of w_I and w_{II} confirms the proposed mechanism.

SUMMARY

1. It is shown that molecular, chain, and radical reactions differ with respect to the concentrations of free radicals.

2. For the identification of chain reactions it is proposed that use should be made of the method of labeled atoms in order to compare the rates of the reaction A → B in absence of B and in presence of an equilibrium concentration of B.

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POSSIBILITY OF THE DETONATION OF GAS MIXTURES IN CONICAL TUBES

S. M. Kogarko

In a previous paper we examined the possibility of initiating a spherical detonation wave in a space containing a gaseous mixture by means of an electric spark, an explosion, or the introduction of a shock wave. In the present paper we report the experimental results of a study of the detonation of gas mixtures in conical tubes and we make a theoretical examination of the conditions under which stable detonation is possible in a tube of constant section, in an infinite space, and in a conical tube.

Let us examine the conditions for the propagation of a stationary detonation wave in a tube of constant section.

It has been established experimentally that, in the propagation of a detonation wave in an explosive mixture contained in a tube of constant section, the wave velocity remains strictly constant over the whole length of the tube. In this case, the constancy of the velocity of the detonation wave is ensured by the constancy of the amplitude of the shock wave that is being propagated in the detonation wave front. On the basis of present-day concepts relating to the processes occurring in a detonation wave, the detonation of a gaseous explosive mixture can be described as follows. A powerful shock wave is propagated through the mixture at the detonation velocity, and this compresses the original mixture so that it attains a high pressure and is raised to a temperature of 1000-2000°. Behind the shock wave there moves a layer l of compressed mixture in which the period of induction for the self-ignition of the mixture τ begins and ends. The length of this layer of the mixture is $l \sim \tau(D - U)$, in which D is the detonation velocity and U is the mass velocity of the gas behind the shock wave. Moving behind the layer of compressed mixture is the reaction zone, in which the explosive chemical reaction is taking place. In this zone the chemical energy of the mixture is evolved and the composition of the mixture changes from its original state at the beginning of the zone to that of the reaction products at the end of the zone. This complex system, consisting of the shock wave, the layer of compressed but not yet reacting mixture, and the reaction zone, moving as a single unit at a constant velocity is the "detonation wave".

In the layer of the mixture compressed by the shock wave, in which the mixture stays during the induction period of self-ignition, no appreciable amount of the chemical energy of the mixture is given up. The compression of the original mixture occurs at the expense of the energy of the shock wave. Owing to the stationary nature of the detonation process, at any given moment the energy being expended by the shock wave in compressing the original mixture must be exactly counterbalanced by the energy entering the shock wave from the reaction zone. We shall assume that the energy expended by the shock wave in compressing the original mixture is proportional to the volume of the compressed mixture. For the detonation of a mixture in a cylindrical tube of constant cross section we may write the volumes of the original mixture that are compressed during two equal periods of time τ, from $t - \tau$ to t and from t to $t + \tau$, in the following form:

$$V_{(t-\tau),t} = \pi r^2 l' \quad \text{and} \quad V_{t,(t+\tau)} = \pi r^2 l',$$

in which l' is the distance traversed by the shock wave through the original mixture during the induction period τ, and r is the radius of the tube.

Let us now write down the ratio of the volume of the original mixture compressed by the shock wave during time τ beginning from the point of time $t - \tau$ to the volume of the original mixture compressed by

the shock wave for the same time τ but beginning from the point of time t. This ratio is the ratio of energies expended by the shock wave in the compression of the original mixture during two successive periods of time τ in the course of the whole process of detonation of the mixture; it will characterize the stability of the shock wave in the detonation process. Let us denote this ratio by H; for a tube of constant section it will be:

$$H = \frac{V_{(t-\tau),t}}{V_{t,(t+\tau)}} = \frac{\pi r^2 l'}{\pi r^2 l'} = 1 \qquad (1)$$

Hence, in the detonation of a gas mixture in a tube of constant section, the energy expended by the shock wave in compressing the original mixture for a period τ will be the same in any two such successive periods, i.e. constant, and therefore the amplitude of the shock wave will also remain constant during the whole detonation process, i.e. the propagation of the shock wave through the mixture will be a stationary process.

The loss of energy from the chemical reaction zone at the walls of the tube resulting from the thermal conductivity of the gas and the friction of the gas against the walls will remain constant during the detonation process and so cannot affect the stability of the detonation wave differently at different times during the detonation of a mixture in a tube of constant section. This loss results in some reduction in the detonation velocity. The experimentally measured detonation velocity is always a few percent below the value calculated from classical detonation theory. The extent of this loss depends on the length of the reaction zone in the detonation wave. This loss increases at the detonation limits, and it results in an appreciable reduction in the detonation velocity. However, before the difference between the theoretically calculated detonation velocity and the experimentally determined value becomes considerable and exceeds 10-15% of the detonation velocity, the limit is reached and the stationary propagation of detonation ceases [1, 2]. Here, we are particularly drawing attention to the fact that the detonation wave can undergo stationary propagation through the mixture when there are losses from the reaction zone corresponding to a reduction in detonation velocity by 10-15% of its theoretical value.

Propagation of a Spherical Detonation Wave

The propagation of a spherical detonation wave through a gaseous explosive mixture will differ fundamentally from the propagation of a detonation wave through a mixture confined in a tube of constant section. As the propagation of a spherical detonation wave proceeds, the surface of the shock wave will increase, and with increase in this surface, the period of induction for self-ignition of the mixture compressed by the spherical shock wave being constant, an increase will occur also in the volume of the original mixture that will be compressed by the spherical shock wave in the period τ. In any given short interval of time the spherical shock wave will always compress a greater amount of the original mixture than in the immediately preceding equal interval, but the spherical shock wave will be supported from the reaction zone by the chemical energy of a mixture compressed in a preceding interval of time; it follows that, in the propagation of a spherical detonation wave, there will always be some weakening of the shock wave. The weakening of the spherical shock wave arises from the lack of equality between the amounts of energy expended by the shock wave on the compression of the original mixture in two successive short intervals of time.

Let us examine what will happen with a spherical shock wave when the mixture is detonated in the center of a large space. At time t let the radius of a shock wave characterized by the same parameters as a plane shock wave formed by detonation of the same mixture in a tube of constant section have the value $r + 1/2\, l'$, in which l' is the length of the layer of original mixture compressed by the spherical shock wave during a time corresponding to the induction period τ for self-ignition of the mixture at the temperature and pressure corresponding to the given shock wave, and r is the average radius of the spherical shock wave for the interval of time from $t - \tau$ to t. The volume of the original mixture compressed by the spherical shock wave in the interval of time from $t - \tau$ to t will be determined by the following equation:

$$V_{(t-\tau),t} = 4\pi r^2 l' .$$

The volume of the original mixture compressed by the spherical shock wave in the interval of time from t to $t + \tau$ will be determined by the following equation:

$$V_{t,(t+\tau)} = 4\pi(\bar{r}+\bar{r}')^2\bar{r}.$$

Assuming, as we did previously, that the energy expended by the shock wave in compressing the original mixture is proportional to the amount of mixture compressed, we may evaluate indirectly the change in the amplitude of the spherical shock wave from one interval of time to the next from the amounts of energy expended by the shock wave in the compression of the original mixture in these two successive intervals of time. Let us write down the ratio of the volumes of the original mixture compressed by the spherical shock wave in the two successive intervals of time $t-\tau$ to t and t to $t+\tau$. This ratio will correspond to the ratio of the energies expended by the shock wave in compressing the original mixture for these two successive intervals of time. Denoting this ratio by H, we obtain

$$H = \frac{4\pi r^2 \bar{r}'}{4\pi \bar{r}'(\bar{r}+\bar{r}')^2} = \frac{r^2}{r^2+2r\bar{r}'+(\bar{r}')^2} = \frac{1}{1+2\frac{\bar{r}'}{r}+\left(\frac{\bar{r}'}{r}\right)^2}. \qquad (2)$$

For all positive values of $\bar{r}'$ and r this ratio will be less than unity. It follows quite obviously that a spherical shock wave will always expend more energy in one interval of time than in the preceding interval. Another, more important conclusion that can be drawn from an analysis of this expression is that the enfeeblement of a spherical shock wave in a mixture of constant period of induction for self-ignition will become less as the radius of the shock wave increases. A third conclusion is that, in different gaseous explosive mixtures having different periods of induction, the spherical shock wave will be enfeebled to the same extent in each mixture not when the radii r of the shock waves are the same, but for a constant value of $\bar{r}'/r$, which is proportional to the ratio that the induction period for self-ignition of the mixture compressed by the spherical shock wave bears to the radius of the shock wave, since $\bar{r}' = \tau D$ (D is the detonation velocity). Hence, when the enfeeblement of the spherical shock wave is still within the permissible limit, within which the breakdown of the spherical detonation wave does not yet occur, the initiation of spherical detonation waves in different gaseous explosive mixtures will be effected by spherical shock waves that will differ both in amplitude and extent.

Every gaseous explosive mixture will be characterized by a minimum critical spherical shock wave capable of initiating the spherical detonation of the mixture. In Fig. 1 the relationship between H, calculated from Equation 2, and $\log \bar{r}'/r$ is shown graphically.

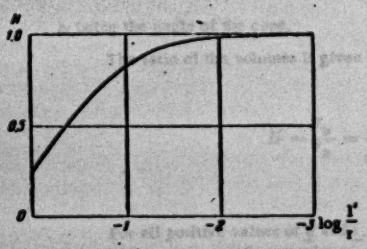

Fig. 1: Dependence of the spherical shock wave on $\bar{r}'/r$.

When spherical detonation of the mixture occurs with some permissible enfeeblement of the spherical shock wave, in the course of the further propagation of the spherical detonation wave its stability should increase. Since the extent of the layer of mixture compressed by the shock wave remains constant in the detonation wave during the whole process of detonation and the radius of the spherical shock wave increases in proportion to the duration of the detonation, the ratio $\bar{r}'/r$ must diminish during the detonation process and the extent of the enfeeblement of the spherical shock wave must also diminish, as will be seen from Fig. 1. Since energy losses from the reaction zone of the detonation wave to the walls of the vessel are absent when spherical detonation of the mixture occurs, it would appear that a spherical detonation wave of high radius should be propagated with smaller losses than those occurring in a plane detonation wave in a tube of constant section, in which losses occur at the walls.

The enfeeblement of the spherical shock wave in the spherical detonation of a gaseous explosive mixture depends not only on the value of the period of induction for self-ignition τ, expressed as the length of the layer of original gas compressed by the shock wave but not yet undergoing reaction, but also on the ratio of the period

of induction to the radius of the spherical shock wave. Hence, in a gaseous explosive mixture for which the period of induction for self-ignition of the mixture compressed by the shock wave is τ and for which detonation is possible in a tube of constant section, it is possible to create a spherical shock wave of radius r such that the ratio l'/r will have less than the critical value. Hence, in a gaseous explosive mixture that is capable of detonation in a tube of constant section, spherical detonation can be initiated under certain experimental conditions.

Propagation of a Detonation Wave in a Conical Tube

From the considerations given above we concluded that, in the propagation of a detonation wave through a mixture in a tube of constant section, the shock wave always compresses the same amount of the original mixture in a given short interval of time τ throughout the whole detonation process. At any given time in the course of the process, the energy expended by the shock wave in compressing the original mixture is precisely counterbalanced by the energy entering the shock wave from the chemical-reaction zone of the detonation wave. What will happen with the shock wave that is propagated in the detonation wave front if we allow the detonation wave, which is undergoing stationary propagation through a mixture in a tube of constant section, to pass into a tube of variable section, i.e. a cone, filled with the same mixture?

Let us write down the ratio of the volume of the original mixture compressed by the shock wave in the time τ required for the detonation wave to move a distance l' along a tube of constant section to the volume of the original mixture compressed by the shock wave in the same interval of time τ when the detonation wave moves a distance l' in the cone. The volume of the original mixture compressed by the shock wave in time τ in the tube of constant section is $V_z = \pi r^2 l'$. The volume of the original mixture compressed by the shock wave in time τ in the cone is

$$V_k = \frac{1}{3}\pi l' [(r+a)^2 + r^2 + (r+a)r] = \pi l' \left(r^2 + ar + \frac{1}{3}a^2\right),$$

where

$$a = l' \tan \frac{1}{2}\alpha$$

α being the angle of the cone.

The ratio of the volumes is given by

$$H = \frac{V_z}{V_k} = \frac{\pi r^2 l'}{\pi l' \left(r^2 + ar + \frac{1}{3}a^2\right)} = \frac{1}{1 + \frac{a}{r} + \frac{1}{3}\left(\frac{a}{r}\right)^2} \qquad (3)$$

For all positive values of a and r, the value of this ratio will always be less than unity. Hence, when the detonation wave passes from a tube of constant section into a cone, the shock wave will be weakened. However, the extent to which it will be weakened may be made as small as we like by suitable choice of the values of a and r. The angle of the cone determines the extent to which the surface of the shock wave increases per unit length, i.e. the extent to which the shock wave is weakened. For every gaseous explosive mixture that is capable of undergoing detonation there is a permissible weakening of the shock wave such that further weakening makes stationary detonation of the mixture impossible; hence, the dimensions of the cone leading from a smaller to a larger tube are not immaterial for the determination of whether a detonation wave will pass from one tube to the other without being broken down.

Experimental Investigation of the Propagation of a Detonation Wave in a Conical Tube

For the investigation of the permissible weakening of the detonation wave the conical tube method was used. In this method, by varying the diameter of the entry tube and the angle of the cone we may vary the extent to which the wave is weakened within wide limits.

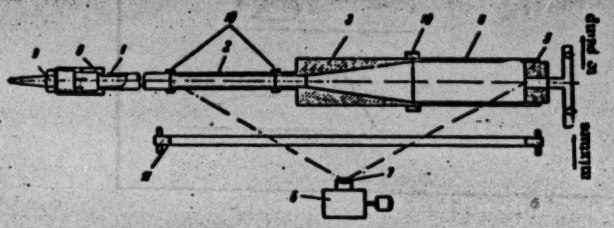

Fig. 2. Diagram of experimental arrangement

A diagram of the apparatus is given in Fig. 2. It consisted of a metal tube 1, 1200 mm in length, a glass tube 2 of the same internal diameter as the metal tube, a metal cone 3, a wide glass tube 4, one end of which was closed by the rubber stopper 5, a recording camera 6 with its objective 7, and connecting tubes for removing reaction products from the apparatus and for filling it with the gaseous explosive mixture under investigation. One end of the metal tube 1 was soldered into the cap 8, which contained the spark plug 9. The metal tube 1 at its open end, the glass tube 2, the metal cone 3, and the wide glass tube 4 were all firmly fixed together at their end surfaces with the aid of short pieces of rubber tubing 10. The part of the apparatus that was filled with the explosive mixture and was shattered in the experiment was separated from the camera by the shield 11, in which a 10-mm slit was made to permit the photoregistration of the propagation of flame in the glass part of the apparatus. The ignition of the mixture was carried out in the metal cap, either by burning a fine copper wire fixed to the electrodes of the spark plug, or, in mixtures highly diluted with nitrogen, by exploding a small amount of lead azide.

The following results were obtained. In the mixture $2H_2 + O_2$, the detonation wave progressed along a tube of internal diameter 5 mm and passed without being broken down through a 5 mm/35 mm cone of angle $\alpha = 11° 30'$ into a tube of internal diameter 35 mm. When the angle of the cone was increased to 23° 0', the detonation wave broke down in a 5 mm/35 mm cone. When the diameter of the first cylindrical tube was increased from 5 to 8 mm, the detonation wave in the $2H_2 + O_2$ mixture passed an 8 mm/38 mm cone of angle $\alpha = 23° 0'$ without breakdown, but was broken down in an 8 mm/38 mm cone of angle $\alpha = 33° 30'$.

Two photorecordings of the propagation of flame fronts through glass tubes placed before and after a cone are shown in Figures 3A and 3B. The photorecordings correspond to the movement of the flame front from top to bottom and the movement of the film from left to right. The upper white band corresponds to the propagation of the flame front and the incandescence of the reaction products in the narrow glass tube placed before the cone, and the lower white band corresponds to the propagation of the flame front and the incandescence of the reaction products in the wide glass tube placed after the cone. The black band sandwiched between the white bands corresponds to the length of the metal cone, in which the flame front is not photographed.

Photorecording 3A corresponds to the propagation of a detonation wave through the mixture $2H_2 + O_2$ in a glass tube of internal diameter 8 mm, followed by an 8 mm/38 mm metal cone of angle $\alpha = 23° 0'$ and a glass tube of internal diameter 38 mm. As can be seen from the photorecording, the detonation wave front is propagated with the same strictly constant velocity both in the 8-mm glass tube and also in the 38-mm glass tube that follows the cone. Detonation velocity in glass tubes was 2790 m per second; average value in cone was 2660 m/sec. Detonation wave propagation rate is reduced in the cone, but the wave is not broken down. Photorecord-

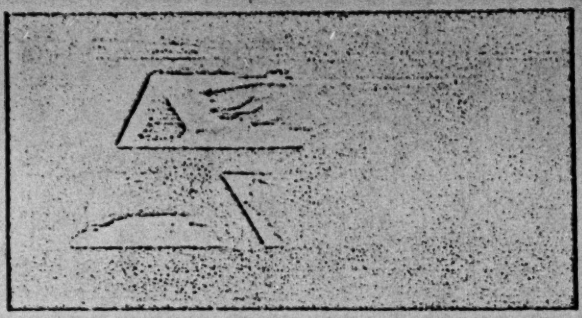

Fig. 3A. Propagation of a detonation wave in glass tubes situated before and after a cone

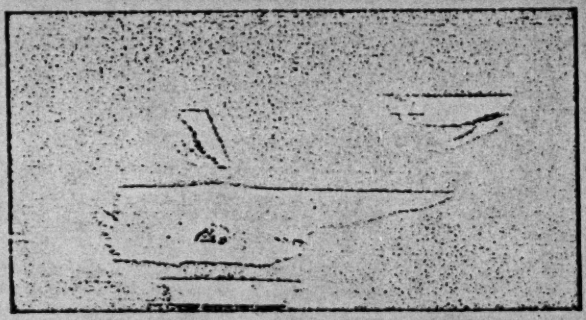

Fig. 3B. Propagation of a detonation wave in glass tubes situated before and after a cone

ing 3B corresponds to a) the propagation of the detonation wave front through the mixture $2H_2 + O_2$ in a glass tube of internal diameter 8 mm; b) the breakdown of the detonation wave in an 8 mm/38 mm cone of angle $\alpha = 33° 30'$; and c) the rapid burning of the mixture in a glass tube of internal diameter 38 mm. It will be clearly seen from the photorecording that the detonation wave is broken down in the cone. The detonation velocity in the 8-mm glass tube was 2760 m per second, and the average velocity of the flame front in the cone was 950 m per second.

The table gives the results of experiments on other mixtures. The pairs of cylindrical glass tubes used in these experiments had diameters of 5 and 35 mm, 8 and 38 mm, and 10 and 40 mm, and the end diameters of the metal cones were 5 mm/35 mm, 8 mm/38 mm, and 10 mm/40 mm.

TABLE

Dimensions of Conical Tubes	5 mm/35 mm		8 mm/38 mm			10 mm/40 mm	
Composition of Mixture	Angle of Cone						
	11°30'	23°0'	23°0'	33°0'	44°0'	11°30'	23°0'
$C_2H_2 + 2.5\ O_2 + 2.5\ N_2$	Detonation	Wave broken down	Detonation	Detonation	Wave broken down	—	—
$C_2H_2 + 2.5\ O_2 + 4.5\ N_2$	Detonation	Wave broken down	DETO	Wave broken down	—	—	—
$C_2H_2 + 2.5\ O_2 + 7.5\ N_2$	Wave broken down	Wave broken down	Wave broken down	Wave broken down	—	Detonation	—
$C_2H_2 + 2.5\ O_2 + 8.75\ N_2$	Wave broken down	Wave broken down	Wave broken down	Wave broken down	Wave broken down	Wave broken down	—
$C_8H_{14} + 9.5\ O_2$	—	—	—	—	—	Detonation	Wave broken down
$C_8H_{14} + 9.5\ O_2 + 19\ N_2$	—	—	—	—	—	Detonation	—
$C_8H_{14} + 9.5\ O_2 + 23.75\ N_2$	—	—	—	—	—	Wave broken down	—
$CH_4 + 2\ O_2$	—	—	—	—	—	Detonation	Wave broken down

Discussion of Experimental Results

The possibility of the spherical detonation of a gas mixture has been examined from the point of view taken by the modern theory of detonation in its treatment of the mechanism of the chemical reaction occurring in a detonation wave produced in a gaseous explosive mixture. The enfeeblement of the spherical shock wave depends both on the size of the spherical detonation wave and on the characteristics of the investigated mixture with respect to reaction kinetics. For a given size of spherical detonation wave the weakening of the spherical shock wave will be the greater, the longer the period of induction for self-ignition of the investigated mixture under the conditions of its compression by the spherical shock wave. When the radius of the spherical detonation wave is sufficiently large, the weakening of the spherical shock wave may, owing to the absence of losses from the reaction zone to the walls of the vessel, be made equal to or less than the weakening of a plane shock wave in the detonation of a mixture in a tube of constant section. It follows from this theoretical result that the spherical detonation of a gaseous explosive mixture is possible.

The weakening of a spherical shock wave depends on the characteristics of the investigated mixture with respect to reaction kinetics and, if it is assumed that the propagation of a stable spherical detonation wave through a mixture becomes possible only when the extent to which the spherical shock wave is weakened is less than a certain critical value that is identical for all gas mixtures (P'/r being constant for any gas mixture), then the critical radius of the spherical shock wave necessary for the initiation of the spherical detonation of the investigated mixture will be the greater, the greater the period of induction for self-ignition of the mixture under the conditions of its compression by the spherical shock wave. It follows that in the experimental determination of the possibility of the spherical detonation of various gaseous explosive mixtures it is impossible to use only one size of spherical shock wave for the initiation. The lack of success that investigators have had in their attempts to initiate spherical detonation in gaseous explosive mixtures is to be explained by the fact that at the time when these experiments were carried out no clear concepts existed concerning the processes occurring in a detonation wave, with the result that the experiments were incorrectly designed. In the experiments of Laffitte [3], attempts were made to bring about the spherical detonation of various gaseous explosive mixtures by the introduction of the plane detonation wave into the investigated mixture from a tube which was of the same dia-

meter in all experiments.

In the investigation of the propagation of a detonation wave through a gaseous explosive mixture contained in a tube of variable section (a cone), it was shown that the detonation wave remains stable when its velocity falls to about 85% of the detonation velocity of the same mixture in a tube of constant section. It is particularly important to note that a plane detonation wave can undergo stable propagation through a mixture not only in a tube of constant section, but also in a tube of variable section so long as the change in the area of the shock wave (due to the change in the cross-sectional area of the tube) produces a weakening in this wave that is within the permissible limit for the given mixture. It follows from these considerations and from the experimental results that we can deliberately change the area of a detonation wave from a small value to any large value that we care to stipulate without destroying the stability of the detonation wave.

SUMMARY

1. It is shown that, in any gaseous explosive mixture capable of being detonated in a tube of constant section, it is possible also to initiate the stationary propagation of a spherical detonation wave.

2. For the initiation of spherical detonation, the critical radius that the spherical shock wave must have will be the greater, the longer the period of induction for self-ignition of the mixture under the conditions of its compression by the spherical shock wave.

3. The relationship derived theoretically between the weakening of the shock wave, on the one hand, and the characteristics of the investigated mixture with respect to reaction kinetics, the geometric dimensions of the wave, and the parameters of the apparatus, on the other, is qualitatively in close accord with experiment.

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PROPERTIES OF ATOMS AT SUPERHIGH PRESSURES

A. F. Kapustinsky

It is difficult to name any law or system in the field of chemistry that is comparable in importance, in wideness of scope, and in the variety of its applications with the periodic law and system of chemical elements proposed by Mendeleev in 1869. All that appeared to be inconsistent with this great generalization was gradually removed as knowledge progressed, whereas all of its consequences received support from experiment, which demonstrated not only the truth of the law, but also its power as a working tool that enables the chemist to predict new facts.

Among the various properties of the elements coming within the scope of the periodic law, from the very beginning the most fundamental were, of course, their chemical properties. However, owing to the various relationships existing between the properties of natural bodies, many physicochemical and even purely physical properties - not only of atoms, but also of molecules and crystals - have been found to be subject in one way or another to the Mendeleev law.

We may draw also chemical thermodynamics into the discussion of this problem, for in this field chemistry is again the principal object of attention, and loss of free energy is a true measure of chemical affinity. Free energy, however, stands in a definite relationship to two other functions of state - enthalpy and entropy. The first of these, known to chemists in the form of the heat of chemical reaction, was the first to be investigated. First Lowry in 1882 and later Mendeleev himself [1] established a periodicity in the heats of formation of chemical compounds; and comparatively recently we have succeeded in establishing a simple, rough thermodynamic logarithmic law [2] which enables the relationship between heats of reaction and the main characteristics of the atoms in the Mendeleev system to be expressed in mathematical form. Still earlier - in 1945 - we discovered the periodicity of ionic and absolute entropies [3], which is interesting in that entropy is the only thermodynamic function of state of which the absolute value is known. We cite here only a few examples that have a certain bearing on the further discussion, but it would be possible to give a very long list of the varied and fruitful applications of the periodic law.

Does this mean that this law (and also the system that is derived from it), in the truth of which there can be no doubt, is some kind of absolute, unconditional fetish that is true everywhere, always, and under all possible circumstances? There are no such absolute laws in chemistry, just as there can be no limit to our knowledge of matter. Like all natural laws, the Mendeleev law has quite definite limitations to its applicability; outside these limits it is no longer applicable. One of our tasks in this short communication is to establish, qualitatively and quantitatively, these limits of applicability.

For this we must first of all remind ourselves of the general line of Mendeleev's discovery: the periodicity of the dependence of the chemical properties of the atoms on one of their physical characteristics, namely on their atomic weights or, more accurately, atomic numbers. The development of this general line led to very fruitful interaction between investigations on the electronic theory of the structure of matter and investigations on the periodic law, and the result was the creation of the electronic theory of atomic structure and of the chemical bond. The periodic system of the elements given below (Fig. 1), which was first proposed by Mendeleev, developed further by Bohr and Thomsen, and somewhat modified by various workers including us [4], expresses the natural classification of atoms according to the structures of their electron envelopes.

It will not be an exaggeration to assert that where there is chemistry there is the periodic law, and where there is Mendeleev periodicity there is also a periodicity in the electronic environments of the atomic nuclei.

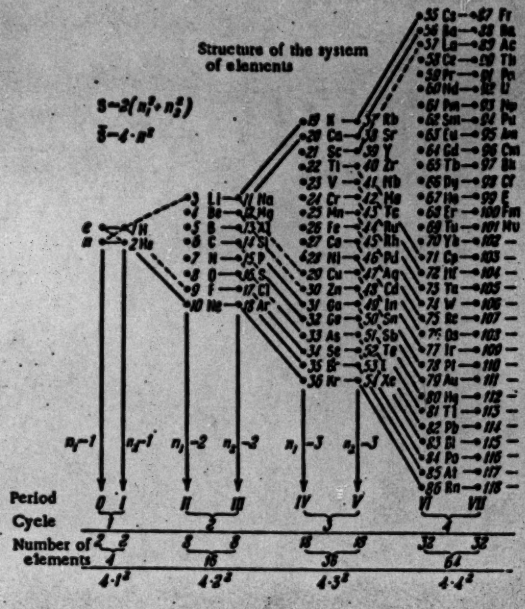

Fig. 1. Stepwise form of the Mendeleev periodic system of the chemical elements.

It follows that for atoms which for some cause or other have lost their correct electronic entourage, the Mendeleev periodic law will not be applicable.

Although this assertion can be regarded as indisputable, if it is not subjected to special examination and investigation it nevertheless remains as nothing more than a mere declaration. It is not difficult to establish the direction that a theoretical investigation must take: it arises quite naturally in the study of the atomic envelopes from the point of view of the Pauli exclusion principle. As is well known, the source of the individuality that is so characteristic of the Mendeleev system is expressed by this principle, which asserts the impossibility for any two electrons in the same atom to have their four quantum numbers identical.

It is well known also, however, that the Pauli principle is not sufficient for the derivation of the periodic law and system. It is necessary to have recourse to the concept of uncompleted electron shells in atoms, as an example of which we may take calcium, for which it is found that it is energetically more favorable for the two outer electrons to go into the fourth energy level, in spite of the possibility in principle for them to go into the third level, which is not yet completed (Table 1).

It appears to be quite possible to transfer these two electrons by external action into the lower orbital 3d. In order to do this it is necessary to apply pressure sufficient to compress the electron envelopes. The electrons will then pass to an orbital that is closer to the nucleus without in any way acting contrary to the Pauli principle. Here an important and interesting question arises: will this treatment alter the chemical nature of calcium as an element? Undoubtedly yes, for its electronic structure will become quite different, as will be seen clearly from Table 2.

Table 1

	1s	2s	2p	3s	3p	3d	4s
Ca_{20}	2	2	6	2	6	—	2

Table 2

	1s	2s	2p	3s	3p	3d	4s
$\overline{Ca}_{20}$	2	2	6	2	6	2	—
Ti^{++}	2	2	6	2	6	2	—

Table 3

	1s	2s	2p	3s	3p	3d	4s
Fe_{26}	2	2	6	2	6	6	2
$\overline{Fe}_{26}$	2	2	6	2	6	8	—
Ni^{++}	2	2	6	2	6	8	—

After the above-described transformation of the atom, its nucleus will remain unaffected - a fact, however, that is irrelevant, since the nucleus takes no part in chemical processes. The number of electrons also remains unchanged. The chemical characteristics will change, however, because both the electron orbitals and the energy of the electrons have changed. For the same electronic "composition", the arrangement of the electrons in space has become different - we meet the phenomenon of electronic isomerism of atoms. We shall refer to the isomer of the calcium atom as "isocalcium" and denote it by $\overline{Ca}$; it already has different, what might be called degenerate, chemical properties. This difference in properties arises from a difference in structure: the localization of the outer electrons in the fourth shell previously resulted in the appearance of the element in the fourth period of the system, whereas the electrons do not now extend beyond the third shell, so that the element must appear in the third period of the system. "Isocalcium" may now be regarded more as an analog of a known titanium ion, as can be seen from Table 2.

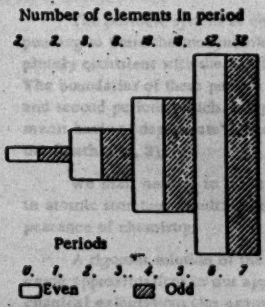

Fig. 2. Diagrammatic representation of the alternation of even and odd periods in the Mendeleev system.

The iron atom provides another curious example of atomic isomerism. In Table 3 we present the normal iron atom, its electronic isomer "isoiron", and its "partial" isomer (only electronic isomerism is present, the nuclear charges being different) or analog of "isoiron" - the ordinary nickel ion.

The electronic isomerization of atoms under pressure is therefore able to alter their chemical properties substantially, for their chemistry is determined by the electronic structure of the outer shells; this is what we have called the degeneration of the chemical properties of the atoms. This peculiar forcing of the electrons into lower, incomplete shells without violation of the exclusion principle - which is possible for elements standing after neon, i.e. beginning from the third period - has, of course, a radical effect both on the properties of the element and, therefore, on its position in the periodic system.

Whereas the well known form of the Mendeleev system with its alternating pairs of even and odd periods and its atoms with incomplete inner shells is divided into seven periods (Fig. 2), the new system of "degener-

ate" atoms must have a much simpler appearance and will contain only five periods instead of seven. At what pressures can such transformations of atoms be brought about? With the aid of the quantum theory of metals developed by Wigner and Seitz Sternheimer [5] calculated the work required for the transfer of an electron from the 6f to the 5d level in the cesium atom. We recalculated his results in terms of pressure and obtained a value of 45,000 atm. Such a pressure is quite realizable, even under laboratory conditions. It is true that for cesium, which has a high atomic radius, this work has its least value; for other atoms it may be 2-3 times as great. Nevertheless, this and other investigations show that for pressures of the order of 50,000-120,000 atm upwards electronic isomerization is quite possible.

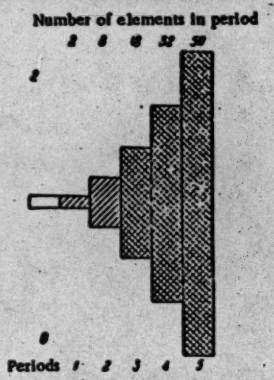

Fig. 3. Diagram of a periodic system containing atoms having degenerate chemical properties (cross-shading).

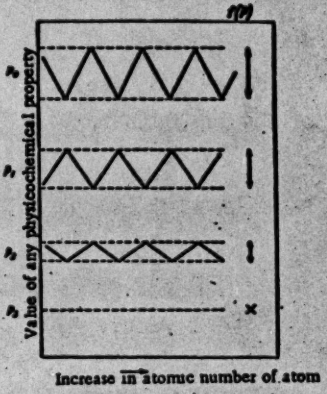

Fig. 4. Diagram of "periodicity function" at various pressures. The values of the "periodicity function" at various pressures are represented by the arrows at the right of the diagram.

The periodic system of chemical elements corresponding to these thermodynamic conditions is still completely consistent with the Pauli principle. The atoms do not contain "vacant" or incomplete quantum levels. The boundaries of these periods (not counting the zero period) will, as before, lie at helium and neon in the first and second periods, which will preserve their normal structures, and then - in the periods corresponding to elements having "degenerate" chemical properties - they will lie at nickel in the third period and at neodymium in the fourth (Fig. 3).

We shall now try to make an approach to the question of the realizability of still deeper transformations in atomic structure, resulting no longer in changes in the chemistry of the elements, but in the complete disappearance of chemistry.

A rigorous solution of the question is again impossible, and existing data enable us to make only very crude approximations in our approach. Even here, however, this approach can be checked - by quantum-mechanical calculations (for example, Ramsey's calculations for hydrogen) and, as we shall see below, by comparison with seismometric data. As usual in geochemistry, we shall use graphs in which pressures are represented on a logarithmic scale, which is always convenient when operating with high numbers; for us, the essential matter is only the obtaining of a more or less smooth curve passing through all points and the plotting of the corresponding seismological data on the same graph - the equation of the curve is immaterial.

In order to answer this question it is necessary to examine the relationship between the periodic changes of various properties and pressure. Unfortunately, our choice of properties is at present extremely limited; there is adequate information on only one property, namely, compressibility.

Richards established periodicity in the relationship between the compressibility of the elements and atomic weight. On the basis of Bridgman's data for 30,000 and 100,000 atm, Vereshchagin and Likhter [6] showed that this periodicity persists up to these high pressures, although it becomes progressively less distinct. This can be best seen from Fig. 4, in which from top to bottom - from low pressures to high - the reduction in the range of the periodicity in the relationship between this property and atomic number is represented in crude diagrammatic fashion. Let us introduce the periodicity function f(P), this being the distance (the arrow on the right in Fig. 4) between the broken lines marking the limits of the variations observed; it may be said to give the "sweep" of the periodic variations. It is clear that the lower the value of this function, the less marked is the periodicity, and its attainment of the value zero corresponds to the complete disappearance of periodicity.

TABLE 4

Pressure p (atm)	Periodicity function f(P)	Logarithm of pressure(log p)	Depth h (km)
1	2.5	0.00	–
30,000	1.3	4.48	–
100,000	0.9	5.00	–
(1,400,000)	0.0	(6.15)	(2,900)

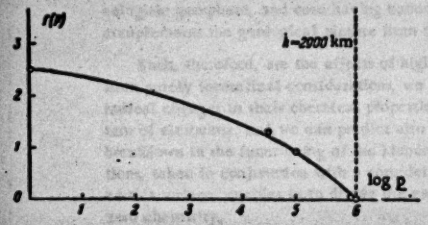

Fig. 5. Graph of the change of the periodicity function with pressure.

Table 4 gives the periodicity function, which we have calculated from Vereshchagin and Likhter's data, in its dependence on pressure, expressed, as already stated, as log p (Fig. 5). We give also the depth below the earth's surface corresponding to a given pressure. Although it is highly probable that a somewhat different picture will be obtained for some property other than compressibility, there is no reason to suppose that the difference will be very great, and the data that we already have may therefore be used in the formulation of certain generalizations.

In Fig. 5 points representing the tabular data lie on a smooth curve, which passes through a point for which the periodicity function has zero value at a pressure of approximately 1,400,000 atm (log p = 6.15). Although this is a very rough extrapolation, in which there may be an error of as much as 100,000 atm, the value will be of the right order. At such pressures, therefore, all chemical properties of matter disappear, the regular layered arrangement of electrons around the atomic nucleus disappears, and we are left merely with "impersonal" nuclei immersed in a general electronic plasma - a universal metallic state of matter.

Can we find any experimental support - if not direct, then at least indirect - of the correctness, with respect to order of magnitude, of our estimates of the quantities under consideration? An answer is found in seismological data.

A study of the passage of seismic waves [7] in different directions through the earth indicates definitely the existence of two important thresholds in the state of matter: a rather diffuse one at a depth of about 100 km corresponding to the thickness of the earth's crust (the so-called Mokhorovichich surface), and another at a depth of 2900 km. The pressure at the first depth ranges from 50,000-100,000 atm, and at the second it is about 1,400,000 atm, in close accord with the estimates that we made by a method quite independent of geophysical and geochemical methods. Inasmuch as homogeneity of phase (more accurately, aggregate invariability) throughout the whole depth of the earth is no longer a matter of doubt, it is difficult to regard this agreement

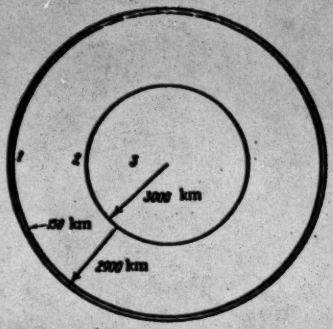

Fig. 6. Zones of the earth: 1) zone of normal chemistry; 2) zone of degenerate chemistry; 3) zone of zero chemistry

otherwise than as confirmation of our estimates of the pressures at which sharp changes occur in the electronic structure of matter. Moreover, from this result we can draw conclusions that are of great importance for geochemistry. It is evident that, in the earth's crust down to a depth of about 100 km, chemical reactions proceed in accordance with the laws we know and the elements follow Mendeleev's periodic system. We have here the geosphere, which may be called the zone of normal chemistry. At greater depths, down to the beginning of the core or centrisphere, pressures are such that the electronic envelopes of the atoms are forced inward to the maximum extent and the properties of the atom are degenerate; this is the zone of degenerate chemistry in which the Mendeleev law in its usual form is already untrue. Finally, there is the core of centrisphere of the earth - the zone of zero chemistry, in which the pressure is so high that no manifestations of chemical properties occur and the periodic system of the elements loses all meaning; only nuclear periodicity is possible. This "geochemical model" of the earth, which is represented in Fig. 6, is in full accord with purely geological concepts of a crust, eclogitic geosphere, and core having boundaries characterized by the same pressures and depths; it therefore complements the geological picture from the viewpoint of chemistry.

Such, therefore, are the effects of high and superhigh pressures on the properties of atoms. In this way, from purely theoretical considerations, we can predict the electronic isomerization of atoms with consequent radical changes in their chemical properties and therefore in the whole structure of Mendeleev's periodic system of elements; and we can predict also the complete annihilation of chemistry, corresponding to complete breakdown in the functioning of the Mendeleev periodic law for the atoms of the elements. These considerations, taken in conjunction with a consideration of the increase in pressure with increase of depth below the earth's surface, enables us to divide the earth into three geospheres - the geospheres of normal, degenerate, and zero chemistry.

This is not all, however; for without confining ourselves to the qualitative side of the solution of the problem, we can now envisage a quantitative approach that will render our solution more precise. Our extremely tentative estimates of the effect of pressure on the structure of electron envelopes correspond in order of magnitude with seismological and geological estimates of the pressures characteristic of the boundaries of these depth zones of our planet - the boundaries of the crust and of the core or centrisphere. In this way we can envisage the possibility of a more or less quantitative estimate of the probable limits of applicability of the Mendeleev periodic law of the elements in nature.

Like every other rigorous and rational limitation of the applicability of a scientific generalization, this one can only consolidate and further confirm this extremely important law of chemistry.

SUMMARY

As the atoms of the elements are compressed under pressures rising to superhigh values, a) at first electrons pass into unfilled levels permitted by the Pauli exclusion principle, with the result that "degeneration" of the normal chemical properties of the atoms occurs and the whole structure of the periodic system of elements changes its form, and b) the "crushing" of the electronic envelopes then occurs with delocalization of electrons, complete loss of the chemical distinctions between the particles, and formation of a universal metallic state of matter.

The paper examines the thermodynamics, quantum-chemical, and seismological data that support the above-stated views, and a hypothesis is advanced concerning the zonal structure of the interior of the earth and the physicochemical properties of the geochemical shells.

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DECOMPOSITION AND FORMATION OF ONIUM SALTS, AND THE SYNTHESIS OF HETEROORGANIC COMPOUNDS

COMMUNICATION 9. HETEROLYTIC DECOMPOSITION OF BENZENEDIAZONIUM FLUOSILICATE

L. G. Makarova and M. K. Matveeva

In previous investigations one of us in collaboration with Nesmeyanov has demonstrated the heterolytic character of the decomposition of benzenediazonium fluoborate in reactions of oriented substitution in the benzene ring [1], in reactions with unsaturated polar compounds [2], and in reactions with nitriles [3]. It may be assumed that benzenediazonium fluosilicate will also decompose heterolytically:

$$(C_6H_5|:N_2)_2|:SiF_6 \longrightarrow 2C_6H_5^+ + N_2 + SiF_6^{--},$$

and this view is supported by the formation of fluoroarenes by the thermal decomposition of arenediazonium fluosilicates [4], which is analogous to Balz and Schiemann's synthesis of fluoroarenes from arenediazonium fluoborates [5]. Moreover, as in the case of arenediazonium fluoborates, the low probability of the formation of a fluorine atom makes a homolytic type of decomposition unlikely.

As in the case of benzenediazonium fluoborates, reactions of oriented substitution in the benzene ring and reactions with nitriles can be applied to the demonstration of the heterolytic character of the decomposition of benzenediazonium fluosilicate. If benzenediazonium fluosilicate undergoes heterolytic decomposition, the phenyl cation formed, being an electrophilic reagent, should substitute in the meta position in a benzene ring containing a meta-orienting substituent, and also, when decomposition occurs in an aromatic nitrile, the phenyl cation may add at the point of highest electron density in the nitrile molecule - at the nitrogen of the nitrile group.

We carried out the decomposition of benzenediazonium fluosilicate in substituted benzenes containing an orienting group of the second kind - in nitrobenzene, methyl and ethyl benzoates, acetophenone, benzonitrile, and phenylacetonitrile. When the decomposition of benzenediazonium fluosilicate was brought about in nitrobenzene, the phenyl cation formed entered the meta position with formation of 3-nitrobiphenyl. Decomposition in ethyl and methyl benzoates yielded 3-biphenylcarboxylic acid after hydrolysis. Phenyl entered not only the meta position with respect to the alkoxycarbonyl group, but also, to a slight extent, the para position, the meta and para isomers being formed in the proportions of about 10 : 1 (for both ethyl and methyl benzoates). The formation of a little para isomer as well as meta is not surprising, for it is known that the alkoxycarbonyl group is only a moderately powerful meta-directing group. When the decomposition took place in benzoic esters, transesterification also occurred with formation of phenyl benzoate, which we interpret as the result of the action of the phenyl cation on the alkoxycarbonyl group.

As in the case of benzenediazonium fluoborate, in the decomposition of benzenediazonium fluosilicate in nitrile media the phenyl cation added to the nitrogen of the nitrile group and anilides of the corresponding acids were obtained when the products were treated with water. When the decomposition was carried out in phenylacetonitrile, 2-phenylacetanilide was obtained in 36% yield, and decomposition in benzonitrile gave benzanilide in 28% yield. Like the decomposition of benzenediazonium fluoborate in nitriles and unlike that of homolytically decomposing diazo compounds [6], the decomposition of benzenediazonium fluosilicate in

nitriles was not accompanied by the formation of ketones or the entry of phenyl into the benzene ring. The formation of nitrile trimers, which arise during the decomposition of benzenediazonium fluoborate in nitriles probably as a result of the polymerizing action of boron trifluoride, was not observed in the decomposition of benzenediazonium fluosilicate in nitriles.

The products of the decomposition of benzenediazonium fluosilicate in acetophenone were the same as those obtained from benzenediazonium fluoborate in the same medium and were different from the products of the decomposition of homolytically decomposing diazo compounds in acetophenone. During the decomposition of benzenediazonium fluosilicate in acetophenone, the phenyl cation entered the benzene ring of the acetophenone. The phenyl cation entered mainly the position meta to the acetyl group, as was shown by the conversion of the corresponding fraction into 3-biphenylcarboxylic acid by the haloform reaction. To a less extent phenyl entered also the para position, and 4'-phenylacetophenone was isolated. The meta and para isomers were obtained in the proportions of 4 : 1. It is again necessary to take the comparative feebleness of the meta-orienting power of the acetyl group into account. In the decomposition of the homolytically decomposing diazo compound potassium phenylazoformate in acetophenone [7] phenyl did not enter the benzene ring, the reaction product being the dimer of the $\cdot CH_2COC_3H_5$ radical, 1,4-diphenyl-1,4-butanedione.

Thus, phenyl formed in the decomposition of benzenediazonium fluosilicate attacks the nitrile molecule at the point of highest electron density - the nitrogen of the nitrile group - and the meta position in a benzene ring containing a meta-orienting substituent (the alkoxyacarbonyl group of a benzoic ester), which indicates the cationoid character of this phenyl and the heterolytic type of decomposition of the diazonium salt that generates it.

EXPERIMENTAL

Decomposition of Benzenediazonium Fluosilicate

The reaction was carried out in a four-necked flask fitted with oil-sealed stirrer, reflux condenser, and thermometer. The fourth neck served for the introduction of the diazonium salt.

a) Decomposition of Nitrobenzene. Over a period of two hours 49 g of benzenediazonium fluosilicate was added in small portions to 150 g of nitrobenzene at 75°. The reaction mixture became dark-colored, the temperature rose slightly, and faint fumes were observed. When the addition of fluosilicate was complete, the temperature was raised to 80° and the reaction mixture frothed slightly for a short time. The mixture was stirred at 79-80° for 45 minutes. On the next day benzene was poured onto the thick dark-colored reaction mixture and a tar separated, which was washed many times with benzene. The benzene extracts were washed with 10% caustic soda (some more resin separated and was filtered off) and with water. They were dried over sodium sulfate, and benzene and nitrobenzene were distilled off, the latter under reduced pressure. Distillation of the residue gave 2.5 g of product, m.p. 150-164 (7 mm). This substance crystallized out completely and, after crystallization from methanol, its melting point and the melting point of a mixture with known 3-nitrobiphenyl were 60°.

b) Decomposition in Methyl Benzoate. The diazonium salt (33 g) was added over a period of 45 minutes to 116 g of methyl benzoate at 105°. Decomposition began immediately with evolution of white fumes. When addition was complete, the mixture was maintained at 150° for one hour. On the next day the reaction mixture was dissolved in ether, and the ether solution was washed with 10% caustic soda and then water. The solution was dried over sodium sulfate, ether was distilled off, and the residue was vacuum-distilled. The following fractions were obtained: Fraction I, b.p. up to 90° (4 mm) (methyl benzoate); Fraction II, 2.48 g, b.p. 125-150°, a liquid; Fraction III, 0.9 g, b.p. 150-165°, which partially crystallized out. Fraction II was hydrolyzed at the boil with 20 ml of 20% aqueous caustic soda for ten hours, some drops of unsaponified oil were extracted with ether, the alkaline layer was acidified with 15% sulfuric acid, excess of concentrated sodium carbonate solution was added, and the mixture was steam-distilled. The distillate gave a feeble reaction for phenol with ferric chloride and bromine water. The alkaline solution was acidified with sulfuric acid, and the precipitate that formed was crystallized from ethanol. The yield was 0.8 g, and the melting points of the product and of a mixture of the product with known 3-biphenylcarboxylic acid were identical (164°).

The precipitate that formed in Fraction III was crystallized from ethanol, and it then melted, both alone

and in mixture with known methyl 4-biphenylcarboxylate, at 117°. The filtrate from Fraction III was hydrolyzed and further treated under the conditions used for Fraction II. A feeble reaction was obtained for phenol in the distillate obtained from the sodium carbonate solution. The residue in the distillation flask was diluted with water, and the undissolved residue was filtered off and boiled with concentrated hydrochloric acid for 15-20 minutes. The precipitate formed was recrystallized from ethanol and then amounted to 0.05 g. Its melting point and the melting point of a mixture of the product with known 4-biphenylcarboxylic acid were identical (222°).

c) Decomposition in Ethyl Benzoate. The diazonium salt (38 g) was added over a period of 40 minutes to 130 g of ethyl benzoate at 105°. Bubbles of gas and white fumes were evolved. When addition was complete, the mixture was stirred at 110° for one hour. It was then dissolved in ether, and the ether solution was washed with 10% caustic soda and with water. The solution was dried with calcium chloride, and the ether and most of the ethyl benzoate were distilled off, the latter under reduced pressure. Vacuum distillation of the residue gave: Fraction I, b.p. 68° (3 mm) (ethyl benzoate); Fraction II, 1.1 g, b.p. 100-130° (3 mm); Fraction III, 3.3 g, b.p. 136-155° (3 mm). Fraction II, after hydrolysis and further treatment under the conditions used for Fraction II in the methyl benzoate experiment, gave a feeble reaction for phenol; the precipitate formed on acidification was found to be benzoic acid. When cooled, Fraction III partially crystallized. The crystals were separated and recrystallized from alcohol, when they amounted to 0.8 g, melting, both alone and in admixture with known phenyl benzoate, at 69-70°.

The oil separated from the crystals was hydrolyzed at the boil with 30% methanolic caustic soda. Methanol was then distilled off, water was added, and the undissolved residue was filtered off, boiled with concentrated hydrochloric acid, and recrystallized from ethanol (yield 0.08 g). Its melting point, alone and in admixture with known 4-biphenylcarboxylic acid, was 222°. The filtrate from the precipitate of sodium 4-biphenylcarboxylate was acidified, and the precipitate formed was recrystallized from petroleum ether and ethanol (yield 1.01 g). Its melting point, alone and in admixture with known 3-biphenylcarboxylic acid, was 163-164°.

d) Decomposition in Benzonitrile. The diazonium salt (38 g) was added over a period of one hour to 74 g of benzonitrile at 80°. The mixture was then maintained at 80° for one hour. The mixture was dissolved in ether, and the solution was washed with 10% caustic soda, when a precipitate formed and was filtered off (Precipitate A). The ether solution was washed with water and dried with calcium chloride. Ether was distilled off, and benzonitrile was distilled off under reduced pressure. Vacuum distillation of the residue yielded: Fraction I, 2.5 g, b.p. 73-166° (3 mm); Fraction II, 7.4 g, b.p. 166-200° (3 mm); Fraction III, 3.02 g, b.p. 255-275° (3 mm).

Fraction I partially crystallized. The crystals were separated from the oil and recrystallized from alcohol (1.3 g, m.p. 163°). Fraction II crystallized completely; after recrystallization from alcohol its melting point, alone and in admixture with known benzanilide, was 163°. Fraction III was a caramel-like viscous mass, from which by crystallization and freezing we succeeded in isolating a further 1 g of benzanilide. Precipitate A (1.5 g, m.p. 163°) was also found to be benzanilide. The total yield of benzanilide was 10.95 g (28%).

e) Decomposition in Phenylacetonitrile. Benzenediazonium fluosilicate (42 g, i.e. 1 mole) was added over a period of 90 minutes to 70 g (5 moles) of phenylacetonitrile at 90°. The reaction mixture immediately became dark-colored, and decomposition proceeded vigorously with evolution of white fumes and nitrogen. The mixture was maintained at 80° for one hour. The mixture was cooled and dissolved in ether. The ether solution was washed with 10% caustic soda solution and with water, and it was then dried over sodium sulfate. Ether and phenylacetonitrile were distilled off, and vacuum distillation of the residue gave: Fraction I, 6 g, b.p. 155-195° (5 mm), and Fraction II, 14.7 g, b.p. 200-240° (5 mm).

Fraction I partially crystallized. The crystals were filtered off and recrystallized from heptane and ethanol (yield 4 g). The melting point of the product, alone and in admixture with known 2-phenylacetanilide, was 114°. Fraction II crystallized completely and melted at 114° after recrystallization from alcohol. The total yield of 2-phenylacetanilide was 18.7 g (36%). Solvent was distilled from the mother liquors from the crystallization of 2-phenylacetanilide, and they were then boiled with concentrated hydrochloric acid for 12 hours. The hydrochloric acid solution was steam-distilled. The distillate was extracted with ether. The ether was distilled off, and the residue was made alkaline and again steam-distilled; the second distillate

was extracted with ether. The extract was dried and ether was distilled off, when a few drops of a viscous oil remained. Treatment of this with 2,4-dinitrophenylhydrazine in ethanol and hydrochloric acid gave a very small amount of a precipitate melting at 231-234° (the 2,4-dinitrophenylhydrazone of deoxybenzoin melts at 204°).

f) Decomposition in Acetophenone. Benzenediazonium fluosilicate (42 g, i.e. 1 mole) was added over a period of 90 minutes to 71.6 g (5 moles) of acetophenone at 75°. During the addition the temperature rose to 80°, and it was maintained at 80° for one hour. The mixture was cooled and dissolved in ether. The ether solution was washed with 10% caustic soda and with water, and it was then dried with sodium sulfate. Ether was distilled off, and most of the acetophenone was distilled off under reduced pressure. Vacuum distillation of the residue gave: Fraction I, 3.5 g, b.p. 75-120° (5 mm); Fraction II, 5.6 g, b.p. 120-205° (5 mm); Fraction III, 6.3 g, 205-265° (5 mm).

Fraction II was again vacuum-fractionated; Fraction I', 0.31 g, b.p. 100-150° (5 mm); Fraction II', 1.63 g, b.p. 157-159° (5 mm); Fraction III', 1.26 g, b.p. 159-160° (5 mm).

A solution of Fraction II' in dioxane was treated with a solution of iodine in alkaline potassium iodide solution. The iodoform formed was filtered off, and dioxane was distilled from the filtrate. When the product was acidified with hydrochloric acid, a precipitate formed and was crystallized from ethanol, when it melted at 162-163°, both alone and when mixed with known 3-biphenylcarboxylic acid. Fraction III' solidified and was crystallized from acetone (yield 0.4 g); its melting point, both alone and in admixture with known 4'-phenylacetophenone, was then 118-119°. Fraction III was subjected to the same haloform scission as Fraction II'. The product was 1.5 g of 3-biphenylcarboxylic acid; after being crystallized from alcohol, it melted, both alone and in admixture with known 3-biphenylcarboxylic acid, at 162-163°. In all, 1.8 g of 3-biphenylcarboxylic acid was obtained.

SUMMARY

1. The phenyl that is formed when benzenediazonium fluosilicate is decomposed in a medium consisting of a benzene derivative containing a meta-orienting group enters the latter in the meta position: in nitrobenzene it gives 3-nitrobiphenyl; in benzoic esters it gives mainly 3-biphenylcarboxylic acid (and also phenyl benzoate); in acetophenone it gives mainly 3'-phenylacetophenone. In benzonitrile and in phenylacetonitrile, the decomposition results in the formation of benzanilide and 2-phenylacetanilide respectively.

2. These reactions prove that the decomposition of benzenediazonium fluosilicate is of the heterolytic type, a phenol cation being formed.

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STRUCTURE OF SOME ORGANIC COMPOUNDS CONTAINING TIN AND PHOSPHORUS

B. A. Arbuzov and N. P. Grechkin

Some years ago, in collaboration with Pudovik we prepared various types of organic compounds containing tin and phosphorus by the action of some alkyltin halides on esters of acids containing tervalent phosphorus [1-4]. Analogous syntheses were carried out by Arbuzov and Pudovik with alkylsilicon halides [5] and by Kamai and Belcronova with alkylarsenic halides [6]. We supposed that the course of these reactions would be analogous to that of the Arbuzov rearrangement, so that the products would contain direct linkages between tin and phosphorus and between silicon and phosphorus.

$$(RO)_3P + R_3SnHal \rightarrow (RO)_2P(O)SnR_3 + RHal \quad (1a)$$

$$2(RO)_3P + R_2SnHal_2 \rightarrow [(RO)_2P(O)]_2SnR_2 + 2RHal \quad (1b)$$

$$PhP(OR)_2 + R_3SnHal \rightarrow \begin{matrix} Ph \\ RO \end{matrix}\!\!>\!P(O)SnR_3 + RHal \quad (2a)$$

$$2PhP(OR)_2 + R_2SnHal_2 \rightarrow \left[\begin{matrix} Ph \\ RO \end{matrix}\!\!>\!P(O)\right]_2SnR_2 + 2RHal \quad (2b)$$

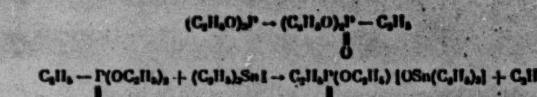
$$Ph_2POR + R_3SnHal \rightarrow Ph_2P(O)SnR_3 + RHal \quad (3a)$$

$$2Ph_2POR + R_2SnHal_2 \rightarrow [Ph_2P(O)]_2SnR_2 + 2RHal \quad (3b)$$

$$(RO)_3P + R_3SiHal \rightarrow (RO)_2P(O)SiR_3 + RHal \quad (4)$$

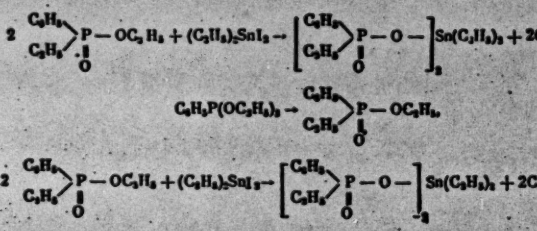
In the decomposition of such products with hydrochloric acid, it was to be expected that alkyltin chlorides would be formed together with phosphorus, phenylphosphonous, diphenylphosphinous acids, respectively. Actually, in all cases we succeeded in isolating the corresponding tin derivatives, but only in the decomposition of the products of reaction (3) did we isolate and identify diphenylphosphinic acid, the formation of which could be explained by the oxidation of the diphenylphosphinous acid originally formed.

In 1950 two papers by Malatesta and coworkers [7, 8] were published, and these express a different view on the course of the reactions (1), (2), (3), and (4) and the structure of the final tin-phosphorus and silicon-phosphorus organic compounds. Malatesta considers that in the reactions of triethyl phosphite with triethyltin iodide and with diethyltin diiodide, and also with bromotriethylsilane, the phosphorous ester is first isomerized into diethyl ethylphosphonite, which then, reacting with the halogen compound of tin or silicon, gives the corresponding mixed triethylstannyl or triethylsilyl ester of ethylphosphonic acid in which tin or silicon is attached to phosphorus through oxygen, for example:

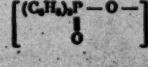


When the same tin derivative reacts with diethyl ethylphosphonate, the same product is obtained, its melting point being undepressed by admixture of the product of the reaction with the phosphorous ester. Only ethylphosphonic acid was isolated from the hydrolysis products.

After checking the results of our previous investigations, we came to the conclusion that Malatesta's views are correct. We hydrolyzed a comparatively large amount of the substance obtained from the reactants given in equation (2b) and obtained a fairly good yield of ethylphenylphosphinic acid, the formation of which is in accord with the course of the reaction proposed by Malatesta and is in conflict with reaction according to the scheme of the Arbuzov rearrangement. When ethyl ethylphenylphosphinate was treated with a dialkyltin dihalide, the product was similar to that of the reaction between diethyl phenylphosphonite and the same tin derivative:



In the case of the reaction of alkyltin halides with ethyl diphenylphosphinite, the Malatesta reaction, with formation of a product containing the P—O—Sn linkage, is impossible because the ester isomerizes into ethyldiphenylphosphine oxide, which does not react with alkyltin halides. After careful purification of the products of the reaction between ethyl diphenylphosphinite and diethyltin dichloride, we concluded that the crystalline product has the structure:



and is formed from ethyl diphenylphosphinate present as impurity in the diphenylphosphinous ester or is formed as a result of an intramolecular oxidation-reduction reaction:

Experiments carried out in order to verify the possibility of such a change did not give positive results. An

attempt to oxidize ethyl diphenylphosphinite into ethyl diphenylphosphinate with oxygen was also unsuccessful.

EXPERIMENTAL

Action of Diethyltin Diiodide on Diethyl Ethylphosphonate. A mixture of 15.4 g (1 mole) of the iodide and 11.8 g (2 moles) of the ester was heated in a flask fitted with a condenser set for distillation. When the temperature of the solution was 125°, ethyl iodide began to distill over, the total amount collected being 8 g (72%). The residue in the flask solidified; the yield (16.9 g) was almost quantitative. Recrystallization from butyl alcohol did not affect the melting point (261-263°), and a mixture test with the substance obtained from the same iodide and triethyl phosphite showed no depression.

Action of Diethyltin Diiodide on Ethyl Ethylphenylphosphinate. Reaction was between 5.2 g (2 moles) of the ester and 5.7 g (1 mole) of the iodide. A solution of the tin compound in the ester was heated in a flask fitted with a condenser set for distillation, and the crystalline residue remaining after distillation of ethyl iodide was washed with a mixture of alcohol and ether. The yield was 5.3 g (78%), and the substance melted with decomposition at 292-294° (measured in a block). There was no depression in a mixture test with the product obtained from diethyl phenylphosphonite and diethyltin diiodide.

Hydrolysis. The substance (3 g) was dissolved in concentrated hydrochloric acid (40 ml). The solution was set aside for 48 hours at room temperature and was then evaporated down several times, first with hydrochloric acid, and then with water until the whole of the hydrochloric acid had been removed. The residue crystallized out; 1.8 g, m.p. 79-80° (from benzene). There was no depression of melting point in a mixture test with a sample of ethylphenylphosphinic acid obtained by the hydrolysis of ethyl ethylphenylphosphinate. Hydrolysis of the organic compound of tin and phosphorus obtained from the phosphonous ester also gave ethylphenylphosphinic acid.

Action of Diethyltin Dichloride on Ethyl Diphenylphosphinite. A mixture of 5.9 g (2 moles) of the ester and 3.18 g (1 mole) of the chloride was heated in an atmosphere of dry nitrogen until ethyl chloride ceased to be evolved; the maximum temperature attained by the solution was 210°. When cooled in a current of nitrogen, the reaction mass crystallized out. After being washed with alcohol and ether, the crystals melted at 346-349° (measured in a block).

	Found %:	C 54.67; 54.66;	H 5.09; 4.95
$C_{28}H_{30}O_4P_2Sn$.	Calculated %:	C 55.00;	H 4.94

Ethyldiphenylphosphine oxide was isolated from the filtrate. When the substance was hydrolyzed with concentrated hydrochloric acid, almost quantitative yields were obtained of diphenylphosphinic acid, m.p. 192-194°, and diethyltin dichloride, m.p. 82-84°.

SUMMARY

On the basis of Malatesta's results and of our confirmatory experiments, it must be considered that the organic compounds of tin and phosphorus under consideration are esters of phosphorus acids in which tin is linked to phosphorus through oxygen.

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REACTION OF O,O-DIALKYL HYDROGEN PHOSPHORODITHIOATES WITH VINYL SULFIDES

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Addition reactions between O,O-dialkyl hydrogen phosphorodithioates and various unsaturated compounds have recently attracted much attention. As shown recently [1], O,O-dialkyl hydrogen phosphorodithioates are relatively strong acids ($K \approx 10^{-2}$), having ionization constants that are much higher than those of most thiols and thio carboxylic acids. Moreover, these compounds are readily oxidized with the formation of compounds containing a disulfide bond [2]. This reaction, which is characteristic of all thiol compounds, indicates the ready formation of thiol radicals. It might be expected, therefore, that O,O-dialkyl hydrogen phosphorodithioates would readily add at double bonds, the mechanism of the reaction being either ionic or free-radical depending on the experimental conditions and the character of the unsaturated compound used. Correspondingly, addition products should be readily formed by reaction both in accordance with and also contrary to Markovnikov's rule.

In some of the papers that have been published on this matter, the structures of the addition products were not proved, in some cases it being assumed that addition proceeded contrary to the rule [3, 4, 5], and in others that it proceeded in accordance with the rule [6]. The question has been investigated in greater detail for the case of reaction between O,O-diethyl hydrogen phosphorodithioate and unsymmetrical olefins [7, 8]. The authors developed a reliable method for proving the structures of the resulting addition products by scission with sodium alkoxide, and they showed that, in the presence of a peroxide, pure O,O-diethyl hydrogen phosphorodithioate adds to 1-octene and to styrene exclusively contrary to Markovnikov's rule:

$$CH_2 = CHR + (C_2H_5O)_2PSSH \xrightarrow{\text{peroxide}} (C_2H_5O)_2PSSCH_2CH_2R. \qquad (1)$$

In absence of peroxides, addition in accordance with the rule can be readily brought about:

$$CH_2 = CHR + (C_2H_5O)_2PSSH \longrightarrow (C_2H_5O)_2PSSCH(CH_3)R. \qquad (2)$$

A catalyst for "normal" addition - which at the same time decomposes peroxides - is the sulfide P_4S_3, which is present in undistilled O,O-diethyl hydrogen phosphorodithioate prepared from alcohol and phosphorus pentasulfide [7, 9]. The presence of this sulfide as impurity explains the "normal" addition of unpurified O,O-dialkyl hydrogen phosphorodithioates to unsymmetrical olefins observed previously by the same authors [8].

It is probably because of their high acidity that O,O-dialkyl hydrogen phosphorodithioates, unlike thiols, have a high rate of uncatalyzed "normal" addition*. In this connection it was considered to be of interest to study the addition of O,O-dialkyl hydrogen phosphorodithioates to the double bond of vinyl sulfides. A study of the ionic reactions of the latter [11] showed that their double bond is somewhat less nucleophilic than that of the strongly nucleophilic vinyl ethers. Vinyl sulfides are however considerably more nucleophilic than unsymmetrical olefins. Nevertheless, some thiols, including benzenethiol, add so readily under normal conditions

* In absence of peroxides, aliphatic thiols, benzenethiol, and thio carboxylic acids either do not add at all to olefins, or add extremely slowly [10].

to vinyl sulfides in the direction contrary to that required by Markovnikov's rule:

$$CH_2 = CHSR' + R''SH \longrightarrow RSCH_2 - CH_2SR', \quad (3)$$

that the occurrence of this reaction forms a substantial obstacle in the synthesis of vinyl sulfides from thiols and acetylene [12-14]. In order to suppress "abnormal" addition of ethanethiol to ethyl vinyl sulfide, considerable amounts of antioxidant must be present. Under these conditions the thiol slowly reacts in accordance with Markovnikov's rule [13].

The reactions between O,O-dialkyl hydrogen phosphorothioates and vinyl sulfides and ethers are referred to in a patent [6]. The authors consider that in both cases addition is in accordance with Markovnikov's rule:

$$CH_2 = CHSR' + (RO)_2PSSH \longrightarrow (RO)_2P(S)SCH(CH_3)SR', \quad (4)$$

but they give no proofs of the structures of their products. Moreover, they do not give the constants of the products and do not indicate the degree of purity of the starting materials.

We have studied the addition of O,O-diethyl and -diisobutyl hydrogen phosphorodithioates to a series of vinyl sulfides, namely, ethyl, butyl, and 2-butoxyethyl vinyl sulfides. All of the reactants were taken in the freshly distilled form, but no special precautions were taken to remove oxygen and traces of peroxides. The reactions were all exothermic, and the only products were O,O-dialkyl S-1-alkylthioethyl phosphorodithioates, which were isolated in 60-80% yield. Hence, addition occurred in accordance with Markovnikov's rule*. The addition of 0.1% of the active free-radical initiator 2,2'-azobis[2-methylpropionitrile] - which effects the abnormal addition of hydrogen sulfide and thiols to alkyl and aryl vinyl ethers [15] - did not affect the direction of the reaction.

All of the products (Table 1) are colorless oily liquids which are very readily superheated in the distillation process. They are readily soluble in various organic solvents. They are oxidized with difficulty by nitric acid.

In order to prove the structure of the products, O,O-diethyl S-1-ethylthioethyl and S-1-butylthioethyl phosphorodithioates were synthesized by a different method which confirmed their structure, namely by the alkylation of potassium O,O-diethyl phosphorodithioate with the corresponding alkyl 1-chloroethyl sulfide:

$$(C_2H_5O)_2PSSK + CH_3CH(SR)Cl \rightarrow (C_2H_5O)_2P\begin{matrix} S \\ \diagdown \\ \diagup \\ SCHSR \end{matrix}\begin{matrix} CH_3 \\ \\ \\ \end{matrix} + KCl, \quad (5)$$

The required alkyl 1-chloroethyl sulfides were prepared by the hydrochlorination of vinyl ethers under the conditions described previously [11]:

$$CH_2 = CHSR + HCl \longrightarrow CH_3 - CH(SR)Cl. \quad (6)$$

The constants of the substances prepared by the two methods were in close agreement (Table 2).

As another method for proving the structure, the reaction with mercuric chloride in an ethanol medium was used. This reaction has been proposed previously for the quantitative determination of monothioacetals [17, 18] and symmetrical mercaptals [13, 19], which are split by the action of mercuric chloride with the elimination of one and two equivalents, respectively, of hydrogen chloride:

* It was established by a special experiment on the reaction between O,O-diethyl hydrogen phosphorodithioate and ethyl vinyl sulfide that an O,O-dialkyl hydrogen phosphorodithioate purified via a salt in accordance with Bacon and le Suer's method [7] also adds to a vinyl sulfide in the direction required by Markovnikov's rule.

TABLE 1

O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates

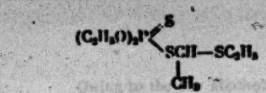
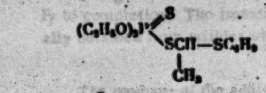
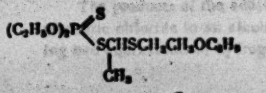
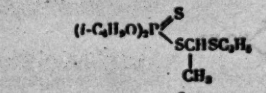
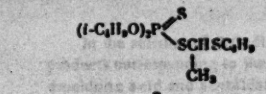
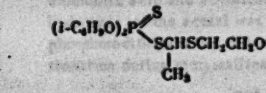
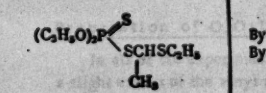
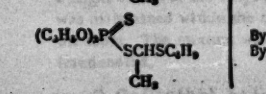
Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Yield (%)
	109—110 (2.5)	1.5290	1.1332	74.18	74.01	70—75
	109—110 (2)	1.5198	1.0965	83.84	83.25	88
	123—125 (3)	1.5125	1.0940	95.10	94.12	80
	113—115 (2)	1.5070	1.0550	93.18	93.49	78
	121—122 (2)	1.5052	1.0384	102.5	102.8	90
	124—126 (3)	1.5012	1.0422	113.8	112.6	60—80

TABLE 2

Specimens of O,O-Diethyl S-1-Alkylthioethyl Phosphorodithioates Prepared by Two Different Methods

Formula of substance	Method of preparation	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
	By addition	109—110 (2.5)	1.5290	1.1332
	By alkylation of salt	109—110 (2.5)	1.5289	1.1391
	By addition	109—110 (2)	1.5198	1.0965
	By alkylation of salt	109—110 (2)	1.5200	1.0969

$$CH_3CH\begin{matrix}SR'\\OR\end{matrix} + HgCl_2 + 2C_2H_5OH \rightarrow CH_3CH(OC_2H_5)_2 + R'SHgCl + HCl + ROH, \quad (7)$$

$$CH_3CH\begin{matrix}SR\\SR\end{matrix} + 2HgCl_2 + 2C_2H_5OH \rightarrow CH_3CH(OC_2H_5)_2 + 2RSHgCl + 2HCl. \quad (8)$$

Owing to the low alcohol-solubility of the alkylthiomercury chlorides formed, the reaction goes practically to completion. The isomeric ethers of 2-mercaptoethanol and 1,2-ethanedithiol give the complex salts usually obtained from sulfides when treated with mercuric chloride, and no hydrogen chloride is eliminated [13, 17].

The products of the addition of O,O-dialkyl hydrogen phosphorodithioates to vinyl sulfides behave toward mercuric chloride in an alcoholic medium as members of a series of phosphorus-containing mercaptals, yielding two equivalents of hydrogen chloride and decomposing according to the equation:

$$CH_3CH\begin{matrix}SR'\\SPS(OR)_2\end{matrix} + 2HgCl_2 + 2C_2H_5OH \rightarrow CH_3CH(OC_2H_5)_2 + 2HCl + R'SHgCl + (RO)_2P(S)SHgCl. \quad (9)$$

In the scission of O,O-diethyl S-1-ethylthioethyl phosphorodithioate with alcoholic mercuric chloride, products corresponding to the above equation were detected. Ethylthiomercury chloride was isolated, and hydrochloric acid and acetaldehyde diethyl acetal were titrated quantitatively. The acetaldehyde obtained by hydrolysis of the acetal was identified as its dinitrophenylhydrazone. As regards the chloromercury O,O-diethyl phosphorodithioate, we did not succeed in isolating it in the pure state owing to the occurrence of disproportionation during recrystallization:

$$2(C_2H_5O)_2PSSHgCl \rightarrow HgCl_2 + [(C_2H_5O_2)PSS]_2Hg. \quad (10)$$

Mercury bis(O,O-diethyl phosphorodithioate) was isolated and identified. Chloromercury O,O-diethyl phosphorodithioate prepared in a known way also underwent the same disproportionation when recrystallized.

The specimens of O,O-dialkyl S-1-alkylthioethyl phosphorodithioates prepared by the two methods reacted in identical manner with alcoholic mercuric chloride.

EXPERIMENTAL

Freshly distilled reactants were used in the experiments. The alkyl vinyl sulfides were prepared from thiols and acetylene [12, 13, 20], and the O,O-dialkyl hydrogen phosphorodithioates were prepared from phosphorus pentasulfide and alcohols and were purified by vacuum fractionation [2, 21].

Preparation of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates

In all of the experiments the O,O-dialkyl hydrogen phosphorodithioate was added dropwise with stirring to a slight excess of the vinyl sulfide, the rate of addition being such that the temperature of the reaction mixture was maintained within the range 60-62°. When addition was complete, the temperature rapidly fell to that of the room. The mixture was stirred for a further 30 minutes and was set aside overnight. It was then vacuum-fractionated.

O,O-Diethyl S-1-Ethylthioethyl Phosphorodithioate. This was prepared from 6.0 g (0.068 mole) of ethyl vinyl sulfide and 9.3 g (0.05 mole) of O,O-diethyl hydrogen phosphorodithioate: b.p. 109-110° (2.5 mm); n_D^{20} 1.5290; d_4^{20} 1.1392; yield 10.0 g (73%).

	Found %:	C 34.78;	34.87	H 6.84;	7.00;	P 11.05;	11.37
$C_8H_{19}O_2PS_2$.	Calculated %:	C 35.01;		H 6.98;		P 11.29	
	Found:	MR 74.18					
	Calculated:	MR 74.01					

O,O-Diethyl S-1-Butylthioethyl Phosphorodithioate. This was prepared from 9.0 g (0.078 mole) of butyl vinyl sulfide and 14.3 g (0.077 mole) of O,O-diethyl hydrogen phosphorodithioate; b.p. 109-110° (2 mm); n_D^{20} 1.5198; d_4^{20} 1.0965; yield 15.5 g (66.2%).

	Found %:	P 10.64;	10.64					
$C_{10}H_{23}O_2PS_2$.	Calculated %:	P 10.25						
	Found:	MR 83.84						
	Calculated:	MR 83.25						

O,O-Diethyl S-1-(2-Butoxyethylthio)ethyl Phosphorodithioate. This was prepared from 10.0 g (0.062 mole) of 2-butoxyethyl vinyl sulfide and 11.0 g (0.059 mole) of O,O-diethyl hydrogen phosphorodithioate; b.p. 123-125° (3 mm); n_D^{20} 1.5125; d_4^{20} 1.0940; yield 16.3 g (80%).

	Found %:	C 41.52;	41.64;	H 7.84;	7.87;	P 8.88;	9.07
$C_{12}H_{27}O_3PS_2$.	Calculated %:	C 41.59;		H 7.86;		P 8.94	
	Found:	MR 95.10					
	Calculated:	MR 94.12					

O,O-Diisobutyl S-1-Ethylthioethyl Phosphorodithioate. This was prepared from 6.0 g (0.068 mole) of ethyl vinyl sulfide and 10.5 g (0.044 mole) of O,O-diisobutyl hydrogen phosphorodithioate; b.p. 113-115° (2 mm); n_D^{20} 1.5070; d_4^{20} 1.0556; yield 11.0 g (77.5%).

	Found %:	C 43.43;	43.20;	H 8.18;	8.15;	P 9.40;	9.51
$C_{12}H_{27}O_2PS_2$.	Calculated %:	C 43.50;		H 8.48;		P 9.30	
	Found:	MR 93.18					
	Calculated:	MR 93.49					

O,O-Diisobutyl S-1-Butylthioethyl Phosphorodithioate. This was prepared from 6.0 g (0.051 mole) of butyl vinyl sulfide and 10.5 g (0.044 mole) of O,O-diisobutyl hydrogen phosphorodithioate; b.p. 121-122° (2 mm); n_D^{20} 1.5052; d_4^{20} 1.0384; yield 13.0 g (91.3%).

	Found %:	C 47.11;	47.11;	H 8.89;	8.86;	P 8.82;	8.83
$C_{14}H_{31}O_2PS_2$.	Calculated %:	C 46.91;		H 8.69;		P 8.64	
	Found:	MR 102.5					
	Calculated:	MR 102.8					

O,O-Diisobutyl S-1-(2-Butoxyethylthio)ethyl Phosphorodithioate. This was prepared from 5.8 g (0.036 mole) of 2-butoxyethyl vinyl sulfide and 7.0 g (0.029 mole) of O,O-diisobutyl hydrogen phosphorodithioate; b.p. 124-126° (3 mm); n_D^{20} 1.5012; d_4^{20} 1.0422; yield 9.0 g (78.2%).

	Found %:	C 47.49;	47.59;	H 8.79;	8.75;	P 7.84;	7.86
$C_{16}H_{35}O_3PS_2$.	Calculated %:	C 47.71;		H 8.76;		P 7.70	
	Found:	MR 113.8					
	Calculated:	MR 112.6					

Synthesis of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates from Alkyl 1-Chloroethyl Sulfides

Preparation of O,O-Diethyl S-1-Ethylthioethyl Phosphorodithioate. In a flask fitted with stirrer, 11.2 g (0.09 mole) of 1-chloroethyl ethyl sulfide was added dropwise to 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorodithioate suspended in 25 ml of dry ether. The temperature rose to 35° and the ether boiled. The reaction was heated in a water bath at 40° for three hours. The precipitate of potassium chloride was filtered off (3.98 g; the theoretical amount was 3.72 g). The filtrate was dried over calcined sodium sulfate and vacuum-fractionated; b.p. 109-110° (2.5 mm); n_D^{20} 1.5289; d_4^{20} 1.1391; yield 8.5 g (62%); found MR 74.30; calculated for $C_8H_{19}O_2PS_2$ MR 74.01.

Preparation of O,O-Diethyl S-1-Butylthioethyl Phosphorodithioate. This was prepared in a similar way from 8.0 g (0.05 mole) of butyl 1-chloroethyl sulfide and 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorodithioate in 20 ml of absolute ether; b.p. 109-110° (2 mm); n_D^{20} 1.5200; d_4^{20} 1.0969; yield 10.8 g (71%); found MR 83.82; calculated for $C_{12}H_{25}O_2PS_2$ MR 83.25.

Reaction of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates with Mercuric Chloride

Reaction of O,O-Diethyl S-1-Ethylthioethyl Phosphorodithioate with Mercuric Chloride. A solution of 2.2 g (0.0081 mole) of mercuric chloride in 11 ml of 96% ethanol was added to 1 g (0.0036 mole) of O,O-diethyl S-1-ethylthioethyl phosphorodithioate. The white precipitate that quickly formed was filtered off after three hours and washed with cold alcohol. The alcohol was added to the filtrate, and the precipitate was vacuum-dried (weight 1.8 g). After the filtrate had stood for five days, a further 0.15 g of crystals came down. Titration of part of the filtrate with standard caustic soda solution gave a hydrochloric acid content of 97.7% of the theoretical value. The filtrate was evaporated to dryness at a residual pressure of 10 mm, the distillate being collected in a trap cooled with dry ice and acetone. Determination of acetaldehyde diethyl acetal in part of the distillate by the hydroxylamine method gave 92.9% of the theoretical value. To the remaining part of the distillate, 0.45 g of dinitrophenylhydrazine and 0.5 ml of concentrated hydrochloric acid were added; the mixture was boiled for 30 minutes and then cooled, when golden needles of acetaldehyde dinitrophenylhydrazone came down (m.p. after recrystallization 163-164°). The weight of the dry residue remaining after the distillation was 0.6 g, reduced to 0.3 g after treatment with water to remove unchanged mercuric chloride. The residue was not treated further since it rapidly turned black. The total weight of mercury salts isolated was 2.25 g (theory requires 2.6 g).

The salts that came down from the solution (1.95 g) were extracted several times with boiling alcohol (75 ml in all). The weight of the residue that remained undissolved was 0.8 g. Recrystallization from boiling xylene [22] gave pearly leaves, which did not melt, but gradually decomposed above 250°.

	Found %:	C 8.40;	8.47;	H 1.82;	2.09
C_2H_5SHgCl	Calculated %:	C 8.08;		H 1.68	

When cooled, the alcohol yielded 0.7 g of fine crystals, which were heated with boiling benzene for one hour in order to complete disproportionation. The decomposition temperature of the crystals that separated from the benzene was 121-121.5°. In admixture with known mercury bis[O,O-diethyl phosphorodithioate] (see below) it melted with decomposition at 121-122°.

	Found %:	C 16.43;	16.57;	H 3.51;	3.40
$C_8H_{20}O_4P_2S_4Hg$	Calculated %:	C 16.82;		H 3.53	

Preparation of Chloromercury O,O-Diethyl Phosphorodithioate $(C_2H_5O)_2PSSHgCl$. An aqueous solution of 13.6 g (0.05 mole) of mercuric chloride was added to an aqueous solution of 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorodithioate. There was an immediate white precipitate, which was filtered off, washed with a large amount of water, and dried. It melted with decomposition at 126-127°; the yield was quantitative.

	Found %:	C 11.67;	11.72	H 2.63;	2.50
$C_4H_{10}O_2PS_2HgCl$	Calculated %:	C 11.40;		H 2.45	

After two recrystallizations from benzene the substance melted at 122-123°, but the carbon and hydrogen contents were greatly increased. After five recrystallizations from benzene the substance had m.p. 121-122° and its composition corresponded to complete disproportionation.

	Found %:	C 16.63;	16.41;	H 3.46;	3.40
$C_8H_{20}O_4P_2S_4Hg$	Calculated %:	C 16.82;		H 3.53	

Preparation of Mercury Bis(O,O-diethyl phosphorodithioate). An aqueous solution of 5.6 g (0.025 mole) of potassium O,O-diethyl phosphorodithioate was added to an aqueous solution of 3.4 g (0.013 mole) of mercuric chloride. A voluminous white precipitate of the mercury compound formed. It was filtered off, washed with water, and dried. The yield was quantitative. After being recrystallized from ben-

zene; it melted with decomposition at 121-122°.

Found %: C 16.48; 16.60; H 3.50; 3.55

$C_8H_{20}O_4P_2S_4Hg$. Calculated %: C 16.82; H 3.53

TABLE 3

Titration of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates $(RO)_2PSSCH(CH_3)SR'$

R	R'	Method of preparation	Equivalent		Content of eliminable S (%)	
			found	calc.	found	calc.
C_2H_5	C_2H_5	Addition of distilled O'O-hydrogen phosphorothioate to ethyl vinyl sulfide	140.8 139.7	137.22	23.91 23.72	23.37
C_2H_5	C_2H_5	Ditto, but with purification of the O,O-diethyl hydrogen phosphorodithioate via the salt [7]	135.2 137.9	137.22	23.02 23.42	23.37
C_2H_5	C_2H_5	Alkylation of potassium O,O-diethyl phosphorodithioate with 1-chloroethyl ethyl sulfide	137.3 135.9	137.22	23.38 23.09	23.37
C_2H_5	C_4H_9	Addition	150.4 148.7	151.25	21.09 20.87	21.20
C_2H_5	C_4H_9	Alkylation	149.8 148.8	151.25	20.99 20.86	21.20
C_2H_5	$CH_2CH_2OC_4H_9$	Addition	172.5 171.4	173.26	18.13 17.96	18.20
i-C_4H_9	C_2H_5	Addition	164.3 165.4	165.25	19.30 19.55	19.40
i-C_4H_9	C_4H_9	Addition	178.4 177.5	179.25	17.84 17.75	17.93
i-C_4H_9	$CH_2CH_2OC_4H_9$	Addition under usual conditions	203.4 197.3	201.3	16.09 15.61	15.93
i-C_4H_9	$CH_2CH_2OC_4H_9$	Addition in presence of 0.1% of 2,2'-azobis[2-methylpropionitrile]	203.1 201.7	201.3	16.07 15.94	15.93

Quantitative Determination of O,O-Dialkyl S-1-Alkylthioethyl Phosphorodithioates

The titration was carried out as already described for monothioacetals [17] and vinyl sulfides [12]. A weighed amount (0.0005-0.001 mole) of O,O-dialkyl S-1-alkylthioethyl phosphorodithioate was placed in a conical flask, and 5-6 times as much (in moles) of mercuric chloride was added as a 20% solution in ethanol. After 1-2 hours the acid liberated was titrated with 0.1 N NaOH to a yellow color with methyl orange. It was found necessary to shake the precipitate well during the titration in order to avoid the formation of mercuric oxide.

The calculated equivalents on the basis of equation (9) and the contents of eliminable sulfur are given in Table 3.

SUMMARY

1. It was shown that O,O-dialkyl hydrogen phosphorodithioates readily add to vinyl sulfides in accordance with Markovnikov's rule.

2. A series of O,O-dialkyl S-1-alkylthioethyl phosphorodithioates were prepared. Their structure was proved by two methods: synthesis from alkyl 1-chloroethyl sulfides, and scission by means of mercuric chloride in ethanol.

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ORGANOBORON COMPOUNDS

COMMUNICATION 8. SYNTHESIS AND PROPERTIES OF DIARYLBORINIC ACIDS

B. M. Mikhailov and V. A. Vaver

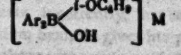
In a previous paper [1] we have described the preparation of diphenylborinic acid and its derivatives. The properties of these compounds and the desire to correct some inaccuracies in data reported in the literature for some other diarylborinic acids prompted us to synthesize a few more representatives of this class of compounds.

We prepared di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chlorophenyl-borinic acids. The isobutyl esters of these acids were isolated in 40-63% yield, together with the corresponding diisobutyl areneboronates, from the reaction products obtained by treating two equivalents of arylmagnesium bromide with one equivalent of triisobutyl borate. The reactions were carried out under the same conditions as those used in the synthesis of isobutyl diphenylborinate [1].

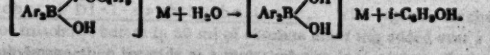
$$2ArMgBr + B(i\text{-}OC_4H_9)_3 \longrightarrow Ar_2B(i\text{-}OC_4H_9) + i\text{-}C_4H_9OMgBr$$

$$Ar = 1\text{-}C_{10}H_7-;\ P\text{-}BrC_6H_4-;\ P\text{-}ClC_6H_4-.$$

A characteristic property of these diarylborinic esters is their stability to hydrolysis by water and dilute mineral acids. A second peculiarity is their ability to dissolve in caustic alkalis with formation, as in the case of isobutyl diphenylborinate [1], of salts of diarylhydroxyisobutoxyboric acids*:



When aqueous solutions of such salts are heated, the alkoxy group of the anion is hydrolyzed with formation of a salt of diaryldihydroxyboric acid:



Barium salts of diaryldihydroxyboric acids are readily prepared by direction treatment of diarylborinic esters with saturated baryta water. It is probable that in this case the same hydrolysis reaction occurs with the anion of the barium salt of the alkoxydiarylhydroxyboric acid, which is formed in the first place, but it proceeds more rapidly as a result of the poor solubility in water of barium salts of diaryldihydroxyboric acids.

* As there is no recognized system of nomenclature for compounds of this type, they are named here by an adaptation of the nomenclature for inorganic complex compounds, "organic" names, however, being given for radicals (e.g. hydroxy, not hydroxo). - Publisher.

Di-1-naphthyl- and bis-p-bromophenyl-boinic esters react readily also with aqueous ammonia, ammonium salts of the corresponding diaryldihydroxyboric acids being formed. Bis-p-chlorophenylborinic esters are exceptional in this respect; they do not react with aqueous ammonia, neither at room temperature nor when heated.

When salts of general formula

$$[Ar_2B(OH)_2]M$$

M = K; Na; $\frac{Ba}{2}$; NH_4; Ar = 1-$C_{10}H_7$–; P-BrC_6H_4–; P-ClC_6H_4–

are treated with acid, they are converted into acids. Salts of dihydroxydi-1-naphthyl- and bis-p-bromophenyldihydroxy-boric acids give the corresponding diarylborinic acids, but salts of bis-p-chlorophenyldihydroxyboric acid, like those of the corresponding diphenyl compound, give a monohydrate of the diarylborinic acid.

Unlike diphenylboiinic acid, the diarylborinic acids now prepared do not form anhydrides when heated in a vacuum, but are converted under these conditions into areneboronic acids with elimination of one aryl radical. Anhydrides can be prepared by treating the acids with thionyl chloride, this being demonstrated for the case of di-1-naphthylborinic acid:

$$(1\text{-}C_{10}H_7)_2B(OH) + SOCl_2 \longrightarrow (1\text{-}C_{10}H_7)_2B\text{–}O\text{–}B(1\text{-}C_{10}H_7)_2.$$

In conclusion, we must discuss data reported in the literature on the diarylborinic acids that we have prepared. Di-1-naphthylborinic acid was isolated recently by Letsinger and coworkers [2], who obtained it by the acid hydrolysis of its aminoethyl ester. As regards the bis-p-bromophenyl- and bis-p-chlorophenyl-borinic acids described by Konig and Scharinbeck [3] and by Melnikov and Rokitskaya [4], it is clear from the method used for the preparation that the authors could not have isolated these substances.

Konig and Scharinbeck, and later Melnikov and Rokitskaya, prepared their organoboron compounds by reaction between equivalent amounts of arylmagnesium bromide and tributyl borate. After treatment of the reaction products with dilute acid and separation of areneboronic acid, at the best the residue could contain a diarylborinic ester, which is not hydrolyzed under these conditions, but it could not contain a diarylborinic acid.

For bis-p-bromophenylborinic acid, Konig and Scharinbeck give m.p. 113°, whereas the acid actually melts at 91°. According to Melnikov and Rokitskaya's results, bis-p-chlorophenylborinic acid corresponds in composition to $(ClC_6H_4)_2B(OH)$, whereas its actual composition corresponds to $(ClC_6H_4)_2B(OH)H_2O$. Moreover, Melnikov and Rokitskaya state, incorrectly, that reaction between equimolecular amounts of tributyl borate and p-chlorophenylmagnesium bromide gives bis-p-chlorophenylborinic acid in 17% yield together with a smaller amount of p-chlorobenzeneboronic acid (15%). We repeated Melnikov and Rokitskaya's experiments and showed that, under their conditions, only p-chlorobenzeneboronic acid is obtained and no bis-p-chlorophenylborinic ester is formed.

EXPERIMENT

Isobutyl Di-1-naphthylborinate. With vigorous mechanical stirring, a solution of 0.225 mole (52 g) of triisobutyl borate in 50 ml of absolute ether was added over a period of 15 minutes to 0.5 mole of 1-naphthylmagnesium bromide as a molar solution in a mixture of ether and benzene, the temperature being maintained at −20° to −30°. When addition of the boric ester was complete, the temperature was lowered, −70° to −75°, and the reaction mixture stirred at this temperature for 6-7 hours. The next day the reaction products were treated with 350 ml 5% HCl. The ether-benzene layer was separated, and the aqueous layer was extracted with ether. The combined ether-benzene extracts were dried with calcined sodium sulfate. After distilling off solvents, a yellowish viscous residue remained; after dilution with 50 ml isopentane, this solidified into a crystalline mass. The reaction product was filtered off under suction, thoroughly washed with isopentane, and vacuum-dried. The product, amounting to 47.5 g (63%) was isobutyl di-1-naphthylborinate, m.p. 104-105° (after recrystallization from hexane).

	Found %:	C 85.20; 85.14;	H 6.73; 6.77;	B 3.17; 3.24
$C_{24}H_{23}BO$	Calculated %:	C 85.22;	H 6.85;	B 3.19

Distillation of solvent from the isopentane filtrate and esterification of the residue with isobutyl alcohol resulted in the isolation of 10 g (15%) of diisobutyl 1-naphthaleneboronate, b.p. 166-168° (6 mm) and d_4^{20} 0.9777.

	Found %:	$C_{10}H_7$	43.70;	43.84;	B	3.60;	3.67
$(C_{10}H_7)B(OC_4H_9)_2$.	Calculated %:	$C_{10}H_7$	44.42;		B	3.78	

Isobutyl di-1-naphthylborinate is a colorless crystalline substance, readily soluble in benzene and chloroform, difficultly soluble in petroleum ether and methanol, and insoluble in isopentane. Diisobutyl 1-naphthaleneboronate is a colorless liquid, readily hydrolyzed - even by atmospheric moisture - into 1-naphthaleneboronic acid.

Ammonium Dihydroxydi-1-naphthylborate. A suspension of 10 g of isobutyl di-1-naphthylborinate in 20 ml of methanol was prepared and was stirred vigorously while 15 ml of 30% aqueous ammonia was added. At first the precipitate dissolved completely, and then a colorless crystalline substance was rapidly precipitated. The mixture was stirred for 30 minutes, and the reaction product was then filtered off at the pump, washed with methanol, and vacuum-dried to constant weight. The product, amounting to 8.85 g (97.5%), was ammonium dihydroxydi-1-naphthylborate, m.p. 105-107°. After recrystallization from methanol the substance melted at 107-108°.

	Found %:	$C_{10}H_7$	79.44;	79.84;	B	3.34;	3.20;	N	4.12; 4.09
$[(C_{10}H_7)_2B(OH)_2]NH_4$.	Calculated %:	$C_{10}H_7$	80.17;		B	3.41;		N	4.41

Ammonium dihydroxydi-1-naphthylborate is a colorless crystalline substance, readily soluble in benzene and hot methanol, difficultly soluble in cold methanol, and insoluble in water. In the air it rapidly decomposes with formation of 1-naphthaleneboronic acid and separation of ammonia and naphthalene.

Di-1-naphthylborinic Acid. A suspension of 4.94 g of ammonium dihydroxydi-1-naphthylborate was prepared in 30 ml of ether, and it was stirred vigorously while 5 ml of dilute (1 : 1) hydrochloric acid was added (acid reaction to Congo red). The ether layer was separated, and the remaining solution was extracted with ether. Ether was removed from the combined extracts under reduced pressure, and the residue was heated at 70° for 10-15 minutes. The reaction product was dissolved in a little dry benzene and reprecipitated with 10 ml of isopentane. The product, amounting to 3.15 g (71.7%), was di-1-naphthylborinic acid, m.p. 113-114°. After being recrystallized from petroleum ether, the di-1-naphthylborinic acid melted at 114.5-115°.

	Found %:	C	84.83;	84.90;	H	5.26;	5.38; B 3.91; 3.97
$C_{20}H_{15}BO$.	Calculated %:	C	85.13;		H	5.35;	B 3.83

Di-1-naphthylborinic acid is a colorless crystalline substance, readily soluble in benzene, difficultly soluble in petroleum ether, and insoluble in isopentane. When it is heated above its melting point in a vacuum, no anhydride formation occurs, but elimination of one of the naphthyls as naphthalene slowly occurs with formation of 1-naphthaleneboronic acid.

Di-1-naphthylborinic Anhydride. A solution of 2 g of di-1-naphthylborinic acid in 5 ml of thionyl chloride was refluxed for two hours. Thionyl chloride was removed under reduced pressure, and the residue was crystallized from a mixture of benzene and petroleum ether. The product, amounting to 1.9 g (98%), was di-1-naphthylborinic anhydride, m.p. 190-192°.

	Found %:	$C_{10}H_7$	91.80;	91.96;	B	4.24;	4.20
$(C_{10}H_7)_2BOB(C_{10}H_7)_2$.	Calculated %:	$C_{10}H_7$	92.98;		B	4.34	

Di-1-naphthylborinic anhydride is a colorless crystalline substance, difficultly soluble in benzene and insoluble in petroleum ether and isopentane.

Isobutyl Bis-p-bromophenylborinate. With vigorous mechanical stirring, a solution of 0.25 mole of triisobutyl borate in 100 ml of absolute ether was added over a period of 30 minutes to 0.65 mole of p-bromophenylmagnesium bromide as a molar ethereal solution (prepared by Fink's method [5]), the temperature being maintained at −30° to −60°. The reaction mixture was stirred at −70° to −75° for eight hours. The reaction products were treated with 450 ml of 5% hydrochloric acid. The residue remaining after removal of ether was esterified with 25 ml of isobutyl alcohol and vacuum-fractionated from a Claisen flask in a current of dry nitrogen. Two fractions were collected, b.p. 102-158° and 158-164° (1 mm) respectively. Further frac-

tionation of the reaction products yielded 38.0 g (39%) of isobutyl bis-p-bromophenylborinate, b.p. 161-163° (1 mm), and 30 g (37%) of diisobutyl p-bromobenzeneboronate, b.p. 109-110° (1 mm) and d_4^{20} 1.1583.

	Found %:	BrC_6H_4 78.73;	78.60;	B 2.65;	2.75	
$(BrC_6H_4)_2B(OC_4H_9)$.	Calculated %:	BrC_6H_4 78.80;		B 2.73		
	Found %:	BrC_6H_4 49.72;	49.81;	B 3.27;	3.31	
$(BrC_6H_4)B(OC_4H_9)_2$.	Calculated %:	BrC_6H_4 49.83;		B 3.46		

Isobutyl bis-p-bromophenylborinate is a colorless, very viscous substance, which slowly solidifies at room temperature. It is soluble in most organic solvents, and it slowly oxidizes in the air. Diisobutyl p-bromobenzeneboronate is a colorless liquid, which is very rapidly hydrolyzed when exposed to the atmosphere with formation of p-bromobenzeneboronic acid.

Ammonium Bis-p-bromophenyldihydroxyborate. Isobutyl bis-p-bromophenylborinate (2.25 g) and 30% aqueous ammonia (5 ml) were shaken together. The crystalline precipitate formed was filtered off at the pump, washed with water, and vacuum-dried to constant weight. The product, amounting to 1.85 g (87.3%), was ammonium bis-p-bromophenyldihydroxyborate, m.p. 133-135°, unchanged by recrystallization from benzene.

	Found %:	BrC_6H_4 83.59;	83.42;	B 2.90;	2.91;	N 3.64;	3.65	
$[(BrC_6H_4)_2B(OH)_2]NH_4$.	Calculated %:	BrC_6H_4 83.23;		B 2.89;		N 3.74		

Ammonium bis-p-bromophenyldihydroxyborate is a colorless odorless crystalline substance, soluble in methanol and ethanol, sparingly soluble in benzene, and insoluble in isopentane.

Potassium Bis-p-bromophenyldihydroxyborate. Isobutyl bis-p-bromophenylborinate (1.23 g) was dissolved in the equivalent amount of aqueous caustic potash (3.65 ml of 0.8 N solution), and water was then slowly distilled off in a current of nitrogen under reduced pressure at 60-70°. The residue was a colorless crystalline substance. After recrystallization from a mixture of benzene with some methanol, 0.8 g was obtained.

	Found %:	BrC_6H_4 78.56;	78.67;	B 2.71;	2.73;	K 9.81;	9.84	
$[(BrC_6H_4)_2B(OH)_2]K$.	Calculated %:	BrC_6H_4 78.80;		B 2.73;		K 9.87		

Potassium bis-p-bromophenyldihydroxyborate is extremely soluble in water and alcohols, but insoluble in benzene, petroleum ether, and isopentane. It is converted quantitatively into bis-p-bromophenylborinic acid by treatment with dilute acids.

Bis-p-bromophenylborinic Acid. Ammonium bis-p-bromophenyldihydroxyborate (1.65 g) was treated with dilute hydrochloric acid. The reaction product was extracted with ether. After removal of ether, the residue was diluted with a little isopentane. The product, amounting to 1.30 g (86%) was bis-p-bromophenylborinic acid. After being recrystallized from petroleum ether the acid melted at 90-91°.

	Found %:	C 42.61;	42.69;	H 2.83;	2.66;	B 3.18;	3.17;	Br 47.38	47.10	
$C_{12}H_9BOBr_2$.	Calculated %:	C 42.41;		H 2.67;		B 3.18;		Br 47.03		

Bis-p-bromophenylborinic acid is a colorless crystalline substance, readily soluble in alcohols and benzene, difficultly soluble in petroleum ether, and insoluble in isopentane. It can be prepared also from potassium bis-p-bromophenyldihydroxyborate (0.899 g of the potassium salt gave 0.760 g of acid, m.p. 87-89°, when acidified); the melting point of a mixture with the analyzed sample of bis-p-bromophenylborinic acid was 89-90°.

Isobutyl Bis-p-chlorophenylborinate. With vigorous stirring, a solution of 0.25 mole of triisobutyl borate in 100 ml of absolute ether was added over a period of 30 minutes to 0.6 mole of p-chlorophenylmagnesium bromide as a molar ethereal solution, the temperature being maintained at −30° to −60°. The reaction mixture was then cooled to a temperature of −70° to −75°, and it was stirred at this temperature for 8-9 hours. On the next day the reaction products were treated with 450 ml of 5% hydrochloric acid. The residue remaining after removal of ether from the combined extracts was esterified with 25 ml of isobutyl alcohol, the alcohol was distilled off, and the residue was distilled rapidly from a Claisen flask (in a current of dry nitrogen). Two fractions were collected: 70-145° and 145-155° (2 mm). Further fractionation of the reac-

tion products through a Hempel column in a current of nitrogen gave 31 g (40%) of isobutyl bis-p-chlorophenylborinate, b.p. 134-135° (1 mm) and d_4^{20} 1.0081.

	Found %:	ClC_6H_4	72.66;	72.23;	B	3.55;	3.53;	Cl 23.27; 23.31
$(ClC_6H_4)_2B(OC_4H_9)$.	Calculated %:	ClC_6H_4	72.66;		B	3.52;		Cl 22.80
	Found %:	ClC_6H_4	41.34;	41.09;	B	3.90;	4.09	
$(ClC_6H_4)B(OC_4H_9)_2$.	Calculated %:	ClC_6H_4	41.53;		B	4.03		

Isobutyl bis-p-chlorophenylborinate is a very viscous colorless liquid; it is immiscible with water, but is soluble in most organic solvents. It is rapidly oxidized in the air. Diisobutyl p-chlorobenzeneboronate is a colorless mobile liquid, miscible with most organic solvents. It is immediately hydrolyzed in the atmosphere with formation of p-chlorobenzeneboronic acid.

Barium Bis-p-chlorophenyldihydroxyborate. Isobutyl bis-p-chlorophenylborinate (1.73 g) was shaken for 5-10 minutes with 15 ml of baryta water (saturated at room temperature). The voluminous precipitate that formed after a few minutes was filtered off at the pump, washed with water, and dried to constant weight. The yield of the salt was 1.7 g (89.5%). Barium was determined by heating a weighed sample of the substance with 1N H_2SO_4, the excess of acid being then titrated with 1N NaOH. Boron and chlorophenyl groups were determined in the usual way on a separate sample.

	Found %:	Ba	20.24;	20.26;	ClC_6H_4	65.58;	65.93;	B 3.14; 3.09
$[(ClC_6H_4)_2B(OH)_2]_2Ba$.	Calculated %:	Ba	20.40;		ClC_6H_4	66.28;		B 3.21

Barium bis-p-chlorophenyldihydroxyborate is a colorless crystalline substance. It is insoluble in water, benzene, and isopentane, but readily soluble in methanol and ethanol. When treated with dilute hydrochloric acid it is converted into bis-p-chlorophenylborinic acid.

Bis-p-chlorophenylborinic Acid. Barium bis-p-chlorophenyldihydroxyborate (2.0 g) was shaken with 10 ml of dilute hydrochloric acid (1 : 4). The emulsion that was immediately formed rapidly turned into a precipitate of a colorless crystalline substance, which was filtered off at the pump, washed with water, and dried over calcium chloride. The substance obtained (1.1 g; m.p. 76-78° after reprecipitation by water from alcohol) corresponded in analysis to the monohydrate of bis-p-chlorophenylborinic acid. When dried in a vacuum it decomposed with elimination of chlorobenzene and formation of p-chlorobenzeneboronic acid.

	Found %:	C	54.53;	54.29;	H	4.49;	4.28;	B 4.08; 3.83; Cl 26.36; 26.66
$C_{12}H_{11}BO_2Cl_2$.	Calculated %:	C	53.58;		H	4.12;		B 4.02; Cl 26.36

The monohydrate of bis-p-chlorophenylborinic acid is readily soluble in benzene, methanol, and ethanol, but insoluble in water.

Sodium Bis-p-chlorophenyldihydroxyborate. Isobutyl bis-p-chlorophenylborinate (2.84 g) was dissolved in the equivalent amount of caustic soda (8.4 ml of 1.09N NaOH). The solution was heated to 60-70°, and water was slowly distilled off under reduced pressure. The residue was washed with benzene and vacuum-dried (yield 2.2 g).

	Found %:	Na	7.42;	7.65;	B	3.53;	3.80	
$C_{12}H_{11}BO_2Cl_2Na$.	Calculated %:	Na	7.90;		B	3.72		

Sodium bis-p-chlorophenyldihydroxyborate is very readily soluble in water and alcohols, but is insoluble in benzene, petroleum ether, and isopentane. On acidification it gives the monohydrate of bis-p-chlorophenylborinic acid, m.p. 72-76° (0.3 g of the salt gave 0.25 g of the monohydrate). A mixture of the product with the analyzed sample of bis-p-chlorophenylborinic acid monohydrate melted at 72-76°.

Boron and aryl groups were determined by Wittig's method [6].

SUMMARY

1. The isobutyl esters of di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chlorophenyl-borinic acids were prepared.

2. It was shown that, when the isobutyl esters of di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chloro-

phenyl-borinic acids were treated with aqueous solutions of caustic soda, caustic potash, ammonia, and barium hydroxide, salts of the corresponding diaryldihydroxyboric acids were formed.

3. Di-1-naphthyl-, bis-p-bromophenyl, and bis-p-chlorophenyl-borinic acids were prepared by treating salts of di-1-naphthyl-, bis-p-bromophenyl-, and bis-p-chlorophenyl-dihydroxyboric acids with dilute hydrochloric acid.

4. It was shown that data reported in the literature for bis-p-bromophenyl- and bis-p-chlorophenylborinic acids are incorrect.

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SYNTHESIS OF ar-CHLORINE-SUBSTITUTED DICHLOROETHYLPHENYLSILANES

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When trichlorophenylsilane is treated with ethylmagnesium bromide, a halogen is readily replaced by an ethyl group with formation of dichloroethylphenylsilane [1]. The reaction between ethylmagnesium bromide and ar-chlorine-substituted trichlorophenylsilanes of various degrees of substitution has not been studied. The replacement of chlorine attached to silicon by ethyl in ar-chlorine-substituted trichlorophenylsilanes is of definite practical and theoretical interest. When ar-chlorine-substituted trichlorophenylsilanes of various degrees of substitution are used in place of trichlorophenylsilane in the reaction with ethylmagnesium bromide, the possibility will arise of the replacement by ethyl not only of chlorine attached to silicon, but also of chlorine present in the aromatic radical. In this paper we give results of a study of the reaction between ethylmagnesium bromide and ar-chlorine-substituted trichlorophenylsilanes.

TABLE 1

Name of substance	Formula	B.p. in °C (p in mm)	d_{20}^{20}	n_D^{20}	MR found	MR calculated
Dichloro(p-chlorophenyl)ethylsilane	$ClC_6H_4(C_2H_5)SiCl_2$	116—118 (7)	1.2947	1.5270	55.06	54.79
Dichloro(2,4-dichlorophenyl)ethylsilane	$Cl_2C_6H_3(C_2H_5)SiCl_2$	130—132 (10)	1.4381	1.5450	58.35	59.23
Dichloro(2,4,6-trichlorophenyl)silane	$Cl_3C_6H_2(C_2H_5)SiCl_2$	142—144 (12)	1.4921	1.5481	64.08	64.07
Dichloroethyl(2,3,4,6-tetrachlorophenyl)silane	$Cl_4C_6H(C_2H_5)SiCl_2$	123—125 (3)	1.5396	1.5618	72.18	69.21
Dichloroethyl(2,3,4,5,6-pentachlorophenyl)silane	$Cl_5C_6(C_2H_5)SiCl_2$	145—147 (3)	1.5896	1.5650	76.82	74.07

Reaction between ethylmagnesium bromide and ar-chlorine-substituted trichlorophenylsilanes was carried out with compounds having different degrees of substitution, namely: trichloro(p-chlorophenyl)silane, trichloro-(2,4-dichlorophenyl)silane, trichloro(2,4,6-trichlorophenyl)silane, trichloro(2,3,4,6-tetrachlorophenyl)silane, and trichloro(2,3,4,5,6-pentachlorophenyl)silane. The experiments showed that ethylmagnesium bromide does not react with chlorines in the aromatic nucleus. When ar-chlorine-substituted trichlorophenylsilanes react with ethylmagnesium bromide under the conditions described above, the chlorine on the silicon atom is replaced by ethyl in accordance with the following scheme:

$$C_2H_5Br + Mg \rightarrow C_2H_5MgBr; \quad (1)$$

$$C_2H_5MgBr + Cl_nC_6H_{5-n}SiCl_3 \rightarrow \begin{matrix} Cl_nC_6H_{5-n} \\ C_2H_5 \end{matrix} \!\!>\!\! SiCl_2. \quad (2)$$

The replacement of halogen by ethyl occurred most readily in trichloro(p-chlorophenyl)silane, dichloro-(p-chlorophenyl)ethylsilane being obtained in about 70% yield. Ethylmagnesium bromide reacted with trichloro(2,4-dichlorophenyl)silane with formation of dichloro(2,4-dichlorophenyl)ethylsilane in 53% yield. Trichloro(2,4,6-trichlorophenyl)silane gave dichloroethyl(2,4,6-trichlorophenyl)silane in 41% yield. Trichloro-(tetra- and penta-chlorophenyl)silanes exchange the chlorine attached to silicon for ethyl much less readily than the mono-, di-, and tri-chlorophenyl compounds.

As a result of the above-described reaction, some new ar-chlorine-substituted dichloroethylphenylsilanes were prepared. Some of their physical properties are given in the table.

EXPERIMENTAL

The ar-chlorine-substituted trichlorophenylsilanes used in the synthesis of ar-chlorine-substituted dichloroethylphenylsilanes were prepared by the chlorination of trichlorophenylsilane, the following procedure being adopted. A mixture of 211 g (1 mole) of trichlorophenylsilane and 1.05 g (0.5% on the weight of the silicon compound) of anhydrous ferric chloride was prepared in a three-necked flask fitted with thermometer, stirrer, and reflux condenser. The mixture was heated to 60°, and chlorine was then passed into the flask at a rate of 0.1-0.2 liter per minute. The course of the chlorination was checked by determining the change in density. During the process the temperature was maintained at 70-80°. Chlorination continued for 10-15 hours. Vacuum fractionation of the reaction product gave trichloro(p-chlorophenyl)silane, b.p. 90-95° (10 mm), d_{20}^{20} 1.4102; trichloro(2,4-dichlorophenyl)silane, b.p. 105-110° (10 mm), d_{20}^{20} 4801; and trichloro(2,4,6-trichlorophenyl)silane, b.p. 123-125° (10 mm), d_{20}^{20} 1.5530.

As the result of still further chlorination we isolated trichloro(2,3,4,6-tetrachlorophenyl)silane, b.p. 135-137° (10 mm), d_{20}^{20} 1.6210, and trichloro(2,3,4,5,6-pentachlorophenyl)silane, b.p. 147-150° (10 mm).

1. Preparation of Dichloro(p-chlorophenyl)ethylsilane. Magnesium turnings (24 g, i.e. 1 mole) were warmed to 36-38° in a three-necked flask fitted with thermometer, stirrer, dropping funnel, and reflux condenser, and 20 g of a mixture of ethyl bromide and ether was dropped in. Reaction soon set in. A mixture of 246 g (1 mole) of trichloro(p-chlorophenyl)silane, 110 g (1 mole) of ethyl bromide, and 100 g of toluene was then added gradually from the funnel, the reaction mixture being stirred vigorously throughout the addition. The reaction temperature was maintained at 38-40°, this being effected by control of the rate at which the addition was made and by periodic cooling of the reaction flask. When the addition was complete, the reaction mixture was heated at 70-80° for two hours with vigorous stirring. The mixture was cooled and was then filtered directly into a distilling flask fitted with a Vigreux column. The precipitate was washed with toluene (weight 135 g). The liquid phase of the reaction product was fractionally distilled; first toluene came over, and then the dichloro(p-chlorophenyl)ethylsilane fraction was separated at reduced pressure, b.p. 116-118° (7 mm), n_D^{20} 1.5270, and d_{20}^{20} 1.2947. The yield was 168 g (70.3%).

	Found %	C	39.51;	38.80;	H	3.73;	3.63;	Si	10.65;	10.41;	Cl	44.8;	44.4
$C_8H_9SiCl_3$	Calculated %	C	40.14;		H	3.78		Si	11.72;		Cl	44.4	

2. Preparation of Dichloro(2,4-dichlorophenyl)ethylsilane. The reaction conditions were the same as those used in the preparation of dichloro(p-chlorophenyl)ethylsilane. Magnesium turnings (12 g, i.e. 0.5 mole) were warmed to 36-38° in the reaction flask and 20 g of a mixture of ethyl bromide and ether was added. A mixture of 140.2 g (0.5 mole) of trichloro(2,4-dichlorophenyl)silane, 55 g (0.5 mole) of ethyl bromide, and 100 g of toluene was then added from the funnel. When the addition was complete, the

reaction mixture was stirred for two hours at 70-80°, and was then cooled, filtered, and fractionated. The product isolated, amounting to 72.5 g (53.7%), was dichloro(2,4-dichlorophenyl)ethylsilane, b.p. 130-132° (10 mm), n_D^{20} 1.5450, and d_{20}^{20} 1.4381.

	Found %:	C	35.86;	35.96;	H	2.95;	2.93;	Si	9.70; 9.59;	Cl 51.9; 51.7
$C_8H_8SiCl_4$.	Calculated %:	C	35.06;		H	2.92;		Si	10.22;	Cl 51.8

3. Preparation of Dichloroethyl(2,4,6-trichlorophenyl)silane. The reaction conditions were the same as those used in the preceding experiments. Magnesium turnings (12 g, i.e. 0.5 mole) were warmed to 36-38° in the reaction flask and 20 g of a mixture of ethyl bromide and ether was added. A mixture of 157.3 g (0.5 mole) of trichloro(2,4,6-trichlorophenyl)silane, 55 g (0.5 mole) of ethyl bromide, and 100 g of toluene was then added. When the addition was complete, the mixture was heated for two hours at 70-80° with vigorous stirring, cooled, filtered, and fractionated. The product, amounting to 63.2 g (41%), was dichloroethyl(2,4,6-trichlorophenyl)silane, b.p. 142-144° (12 mm), n_D^{20} 1.5481, and d_{20}^{20} 1.4921.

	Found %:	C	31.1;	31.5;	H	2.72;	2.63;	Si	9.63; 9.43;	Cl 56.9; 57.0
$C_8H_7SiCl_5$.	Calculated %:	C	31.14;		H	2.27;		Si	9.07;	Cl 57.5.

4. Preparation of Dichloroethyl(2,3,4,6-tetrachlorophenyl)silane. The reaction conditions were the same as those used in the preceding experiments. Magnesium turnings (12 g, i.e. 0.5 mole) were placed in the flask, 20 g of a mixture of ethyl bromide and ether was added, and then a mixture of 175 g (0.5 mole) trichloro(2,3,4,6-tetrachlorophenyl)silane, 55 g (0.5 mole) ethyl bromide, and 100 g toluene was added. When addition was complete, mixture was heated for 2 hours, cooled, and filtered. Toluene was distilled off, and the residue fractionated. The product, 51.4 g (30%), was dichloroethyl(2,3,4,6-tetrachlorphenyl)silane, b.p. 123-125° (3 mm), n_D^{20} 1.5618; d_{20}^{20} 1.5396.

	Found %:	C	26.96;	27.03;	H	2.22;	2.18;	Si	8.33; 8.09;	Cl 61.72 61.82
$C_8H_6SiCl_6$.	Calculated %:	C	28.01;		H	1.75;		Si	8.17;	Cl 62.0

5. Preparation of Dichloroethyl(2,3,4,5,6-pentachlorophenyl)silane. The reaction conditions were similar to those used in the preceding experiments. Magnesium turnings (2 g, i.e. 0.08 mole) were warmed to 36-38° in the reaction flask, and 2 g of a mixture of ethyl bromide and ether was then added. After this "starter", a mixture of 30 g (0.08 mole) of trichloro(2,3,4,5,6-pentachlorophenyl) silane, 10 g (0.08 mole) of ethyl bromide, and 30 g of toluene was added. When the addition was complete, the reaction mixture was stirred at 70-80° for two hours, cooled, and filtered. Toluene was distilled off, and the residue was fractionated. The product, amounting to 7 g (23%), was dichloroethyl(2,3,4,5,6-pentachlorophenyl)silane, b.p. 145-147° (3 mm), n_D^{20} 1.5650; d_{20}^{20} 1.5996.

	Found %:	C	27.38;	27.35;	H	2.16;	2.35;	Si	7.47; 7.74;	Cl 63.25; 63.62
$C_8H_5SiCl_7$.	Calculated %:	C	25.45;		H	1.32;		Si	7.42;	Cl 65.79

SUMMARY

1. The reaction between ethylmagnesium bromide and ar-chlorine-substituted trichlorophenylsilanes was studied.

2. The following new compounds were prepared: dichloro(p-chlorophenyl)ethylsilane, dichloro(2,4-dichlorophenyl)ethylsilane, dichloroethyl(2,4,6-trichlorophenyl)silane, dichloroethyl(2,3,4,6-tetrachlorophenyl)silane, and dichloroethyl(2,3,4,5,6-pentachlorophenyl)silane.

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WURTZ SYNTHESIS OF ORGANOSILICON COMPOUNDS HAVING A DOUBLE BOND IN THE α-POSITION

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Sodium has been applied successfully in the synthesis of aromatic and aliphatic-aromatic silanes from $SiCl_4$ or R_nSiCl_{4-n} and ArX [1], but the applicability of this reaction to the synthesis of aliphatic silanes was found to be limited owing to the fact that low yields were often obtained. For example, tetraethylsilane is obtained in low yield by this reaction, and tetraallylsilane is not formed at all [2].

Until recently, vinyl halides and their derivatives have not been applied in the Wurtz reaction. The preparation of organosilicon compounds having a double bond in the α-position with respect to silicon has been effected by direct synthesis [3], by elimination of HCl from chlorinated organosilicon compounds [3-5], by addition of $HSiCl_3$ to acetylenic hydrocarbons [6], and in other ways.

These compounds were not synthesized by the organometallic method because, with the exception of β-bromostyrene, vinyl halides and their derivatives could not be converted sufficiently simply and in good yield into Mg, Li, or Na derivatives. Only recently was it found that 2-methylpropenyl bromide [7] and isopropenyl bromide [8] form organolithium compounds of adequate stability, and these were applied by Petrov and Nikishin [8] in the synthesis of a series of 1-alkenylsilanes.

Finally, in 1953 Kanazashi [9] condensed various chloroalkylsilanes with vinyl chloride with the aid of sodium activated by ethyl acetate. He prepared dimethyldivinylsilane and a series of trialkyl(or aryl)vinylsilanes. In the present investigation we found that Kanazashi's procedure is general for the condensation of chlorosilanes not only with vinyl chloride, but also with its derivatives, i.e. compounds having the grouping $>C=CCl$. It must be pointed out that our attempts to carry out the reaction with compounds of the type of allyl and 2-propynyl chlorides were not successful. Condensation of vinyl chloride with $SiCl_4$, even with the latter in excess, gave only one product, tetravinylsilane; no chlorovinylsilanes could be isolated. From 2-methylpropenyl and propenyl bromides we synthesized ethyldimethyl(2-methylpropenyl)silane and ethyldimethylpropenylsilane respectively:

$$(CH_3)_2C{=}CHBr + ClSi(CH_3)_2C_2H_5 \xrightarrow{Na} (CH_3)_2C{=}CHSi(CH_3)_2C_2H_5;$$

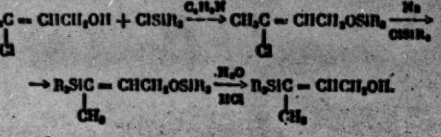
$$CH_3CH{=}CHBr + ClSi(CH_3)_2C_2H_5 \xrightarrow{Na} CH_3CH{=}CHSi(CH_3)_2C_2H_5.$$

The preparation of compounds of this type by the Wurtz reaction is simpler than the organolithium synthesis and does not require excess of the alkenyl bromide [8]. By reaction of (1-chlorovinyl)- and (2-chlorovinyl)-trimethylsilanes with $(CH_3)_3SiCl$, good yields were obtained of 1,1- and 1,2-bistrimethylsilylethylenes, i.e. 2,2,4,4-tetramethyl-3-methylene-2,4-disilapentane and 2,2,5,5-tetramethyl-2,5-disilahex-3-ene:

$$(CH_3)_3SiCCl{=}CH_2 + ClSi(CH_3)_3 \xrightarrow{Na} (CH_3)_3Si\underset{\displaystyle CH_2}{\overset{\displaystyle |}{C}}Si(CH_3)_3;$$

$$(CH_3)_3SiCH{=}CHCl + ClSi(CH_3)_3 \xrightarrow{Na} (CH_3)_3SiCH{=}CHSi(CH_3)_3.$$

Finally, from 3-chloro-3-methylallyl alcohol (3-chloro-2-buten-1-ol), which is readily prepared from 1,3-dichloro-2-butene, 3-(trialkylsilyl)-2-buten-1-ols were prepared by the reactions given below (R = CH_3 and C_2H_5):



These first unsaturated organosilicon alcohols are readily cyanoethylated with acrylonitrile. The fact that, under the conditions of the Wurtz synthesis, tetravinylsilane is obtained in 65% yield, whereas tetraallylsilane is not obtained at all, is not difficult to understand in view of Petrov and Shchukovskaya's recent observation [10] that phenyllithium breaks the Si–C link in allyltriphenylsilane. It is evident that allylsodium formed under the conditions of the Wurtz synthesis, also breaks the Si–C link in tetraallylsilane.

TABLE

No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Yield (%)
1	$Cl_2SiCH_2CH_2Cl$	151.7 (751)	1.4652	1.4239	38.45	38.64	93
2	$Cl_2SiCHClCH_3$	136.5 (746.5)	1.4545	1.3912	38.56	38.64	
3	$Cl_2SiCHClCH_2Cl$	180 (755)	1.4850	1.5156	43.94	43.48	—
4*	$Cl_2SiCClSiCl_3$ CH_2	224 (741)	1.4972	1.5926	60.90	61.05	44
5	$Cl_2SiCH=CHCl$	133 (731)	1.4745	1.4364	38.37	38.17	60
6	$Cl_2SiCCl=CH_2$	124 (740)	1.4648	1.4243	38.01	38.17	
7*	$Cl_2SiCSiCl_3$ CH_2	199—200 (740)	1.4930	—	—	—	—
8*	$(CH_3)_2SiCH=CHCl$	116.6 (741)	1.4380	0.8924	39.61	39.28	77
9*	$(C_2H_5)_2SiCCl=CH_2$	182—3 (739)	1.4595	0.9186	52.64	52.81	78.5
10*	$(CH_3)_2SiCH=CHSi(CH_3)_3$	145.0 (746)	1.4310	0.7589	58.79	57.96	89.5
11*	$(CH_3)_3SiCSi(CH_3)_3$ CH_2	151.6 (756.5)	1.4374	0.7823	57.76	57.96	46.5
12*	$Si(CH=CH_2)_4$	130.2 (746.1)	1.4625	0.7909	48.87	46.92	65
13*	$C_2H_5(CH_3)_2SiCH=CHCH_3$	118.5 (739)	1.4263	0.7546	43.50	43.58	32.5
14*	$C_2H_5(CH_3)_2SiCH=C(CH_3)_2$	139.5 (743)	1.4361	0.7649	48.64	48.68	50.1
15*	$(CH_3)_3SiOCH_2CH=CCICH_3$	164—5	1.4350	0.9481	49.18	49.30	50.8
16*	$(CH_3)_3SiOCH_2CH=CSi(CH_3)_3$ CH_3	195 (759)	1.4369	0.8309	68.22	67.98	52
17*	$(CH_3)_2SiC=CHCH_2OH$ CH_3	47 (2)	1.4590	0.8693	45.34	45.25	60
18*	$(C_2H_5)_2SiC=CHCH_2OCH_2CH_2CN$ CH_3	113 (2)	1.4732	0.9215	72.90	72.71	85
19*	$(C_2H_5)_2SiOCH_2CH=CCICH_3$	72 (2)	1.4538	0.9553	62.56	62.83	83.5
20*	$(C_2H_5)_2SiOCH_2CH=CSi(C_2H_5)_3$ CH_3	101 (2)	1.4628	0.8716	94.98	95.04	52
21*	$(C_2H_5)_2SiC=CHCH_2OH$ CH_3	81 (2)	1.4725	0.8886	58.77	58.78	59
22*	$(CH_3)_2SiC=CHCH_2CH_2OCH_2CH_2CN$ CH_3	65 (6)	1.4610	0.9153	59.15	59.24	80

* Prepared for the first time.

The synthesis of tetraallylsilane has enabled us to establish that, unlike allyl [11], vinyl attached to silicon does not show exaltation of molecular refraction. A comparison of the Raman spectra of tetravinylsilane and triethylvinylsilane enabled the most characteristic frequencies of vinyl attached to silicon to be determined; 1272, 1404, 1594, and 3054 cm^{-1}. It was found also that the intensities of these lines increase in proportion to the number of vinyl groups, i.e. for $(CH_2{=}CH)_4Si$ they are four times as intense as for $(C_2H_5)_3SiCH{=}CH_2$. Similar behavior was observed previously for allylsilanes [11]*. It is interesting also to note that tetravinylsilane combines more slowly than $(C_2H_5)_3SiCH{=}CH_2$ with thiocyanogen.

The table gives the properties both of compounds prepared previously but now characterized in greater detail and also of compounds now synthesized for the first time.

EXPERIMENTAL

Tetravinylsilane $(CH_2{=}CH)_4Si$ (I). Sodium (140 g) was melted under 500 ml of toluene in a one-liter flask fitted with reflux condenser, dropping funnel, tube reaching to the bottom for the passage of gas, and stirrer. The sodium was converted into the state of dust by rapid rotation of the stirrer. The toluene was cooled and decanted from the sodium, and 300 ml of ether and 250 g of $SiCl_4$ were introduced into the flask. Ethyl acetate (3-5 ml) was then added, and vinyl chloride (dried with phosphoric oxide) was passed through the stirred mixture so that the ether boiled gently. After seven hours, the precipitate was filtered off, ether was distilled from the filtrate, and the residue was vacuum-distilled (b.p. 66-68° at 90 mm). Redistillation through a column gave 70 g of (I), b.p. 120-130°, in 65% yield.

	Found %	C	70.49;	70.71;	H	8.91;	8.92;	Si 20.82; 20.71
$C_8H_{12}Si$.	Calculated %	C	70.52;		H	8.88;		Si 20.60

$\Delta\nu$: 305(20b), 343(15), 584(35), 734(5), 962(12), 1010(12b), 1271(90), 1404(150), 1594(160), 2846(15), 2950(35), 2674(325), 3009(20), 3054(125).

Chlorination of $C_2H_5SiCl_3$, $ClCH_2CH_2SiCl_3$ (II), $CH_3ClCHSiCl_3$ (III), and $Cl_3SiCHSiCl_3$. Chlorination was carried out under ultraviolet irradiation under the conditions described previously [12]; it appeared to proceed in the liquid phase since liquid-drop condensation of the substance being chlorinated occurred in the reaction zone. In the chlorination of 2 kg of $C_2H_5SiCl_3$, a 93% yield was obtained of the compounds (II) and (III) in the proportions 1 : 1.5. In the chlorination of (III) at a temperature in the flask of up to 152°, an 89% yield was obtained of trichloro(1,1-dichloroethyl)silane (IV) and trichloro(1,2-dichloroethyl)silane (V) in the proportions 1 : 0.6. The chlorination of (II) at temperatures ranging up to 174° gave a difficultly separable mixture of (V) and trichloro(2,2-dichloroethyl)silane (VI), b.p. 170-180°, in 93% yield. The chlorination of $Cl_3SiCHSiCl_3$ (CH_3) gave a 44% yield of $Cl_3SiCClSiCl_3$ (CH_3) (VII), b.p. 199-200°.

	Found %	C	7.43;	7.24;	H	0.98;	0.91;	Si 17.47; 16.93; Cl 73.83; 73.83
$C_2H_3Si_2Cl_7$.	Calculated %	C	7.27;		H	0.61;		Si 16.99; Cl 75.12

The elimination of HCl from (IV), (V), the mixture of (V) and (VI), and (VII) was carried out by distilling them with quinoline [5] or with diethyl- or dimethyl-aniline and then redistilling the distillate through a column. It is more convenient to use diethyl- or dimethyl-aniline rather than quinoline, since these compounds do not form volatile salts that cause breakages in the apparatus and do not give solid residues that are difficult to remove from the flask. The mixture of (V) and (VI) gave a 60% yield of $Cl_2SiCH{=}CHCl$ (VIII) and $Cl_2SiCCl{=}CH_2$ (IX) in the proportions 1 : 1.3.

(1-Chlorovinyl) trimethylsilane [5] $CH_2{=}ClCSi(CH_3)_3$ (X). The compound (IX) (100 g) was added over a period of an hour to CH_3MgI prepared from 45 g of Mg and 350 g of CH_3I in 500 ml

*The spectra were determined and interpreted by Yu. P. Egorov.

of ether. The mixture was boiled for five hours, and on the next day it was decomposed with water. Ether was removed from the ether layer, and distillation of the residue through a column gave 42 g (61.5%) of the compound (X), b.p. 104°. Color due to the presence of iodine was removed by means of aqueous sodium sulfite solution.

(2-Chlorovinyl) trimethylsilane $ClCH=CHSi(CH_3)_3$ (XI). The compound (VIII) (48 g) was added over a period of two hours to CH_3MgI prepared from 18.5 g of Mg and 140 g of CH_3I in 500 ml of ether. The mixture was boiled for five hours, and the usual treatment and distillation through a column gave 25 g (77%) of the compound (XI), b.p. 114-116°.

	Found %:	C	44.73;	44.6;	H	8.33;	8.30;	Si	20.63; 20.45; Cl 26.80; 25.70
$C_5H_{11}SiCl$.	Calculated %:	C	44.59;		H	8.31;		Si	20.83; Cl 26.33

(1-Chlorovinyl) triethylsilane $CH_2=ClCSi(C_2H_5)_3$ (XII). The compound (IX) (189 g) was added to C_2H_5MgBr prepared from 77 g of Mg and 420 g of C_2H_5Br in 1500 ml of ether. On the next day, after a two-hour boil and the usual treatment, 133 g (78.5%) of the substance (XII), b.p. 183°, was obtained.

	Found %:	C	54.06;	54.10;	H	9.63;	9.64;	Si	16.14; 15.97
$C_8H_{17}SiCl$.	Calculated %:	C	54.36;		H	9.69;		Si	15.87

2,2,4,4-Tetramethyl-3-methylene-2,4-disilapentane $[(CH_3)_2Si]_2C=CH_2$ (XIII). Sodium (9 g) was melted under 30 ml of toluene and converted by stirring into fine dust. The mixture was cooled, and 500 ml of ether, 20 g of $(CH_3)_2SiCl$, 1.2 ml of (X), and 1.2 ml of ethyl acetate were added. When reaction had set in, 23.5 g of (X) was added at such a rate that the ether boiled gently. The mixture was then heated for 2.5 hours. The precipitate was filtered off, ether was distilled from the filtrate, and the residue was distilled through a column and gave 14 g (46.5%) of (XIII), b.p. 151°.

	Found %:	C	55.97;	55.99;	H	11.50;	11.58;	Si	32.55; 32.67
$C_9H_{22}Si_2$.	Calculated %:	C	55.74;		H	11.69;		Si	32.55

2,2,5,5-Tetramethyl-2,5-disilahex-3-ene $(CH_3)_2SiCH=CHSi(CH_3)_3$ (XIV). Sodium (10 g) was granulated in isooctane, 250 ml of ether was added, and to the suspension so obtained 25 g of $(CH_3)_2SiCl$ and 2 ml of (XI) were added. Reaction was initiated by addition of 1-2 ml of ethyl acetate, and 27 g of (XI) was then added. The mixture was boiled for four hours, and the precipitate formed was filtered off. The product, amounting to 34 g (76%), was the compound (XIV).

	Found %:	C	56.06;	55.99;	H	11.82;	11.69;	Si	32.59; 32.35
$C_9H_{22}Si_2$.	Calculated %:	C	55.74;		H	11.69;		Si	32.55

Ethyldimethyl (2-methylpropenyl) silane $C_2H_5(CH_3)_2SiCH=C(CH_3)_2$ (XV). To 17 g of sodium in 250 ml of ether, 41 g of $C_2H_5(CH_3)_2SiCl$ and 1 ml of ethyl acetate were added. 2-Methylpropenyl bromide (47 g) was then added gradually. The usual treatment gave 23.8 g (50.1%) of (XV).

	Found %:	C	67.74;	67.56;	H	12.75;	12.58;	Si	19.71; 19.54
$C_8H_{18}Si$.	Calculated %:	C	67.52;		H	12.75;		Si	19.72

Ethyldimethylpropenylsilane $C_2H_5(CH_3)_2SiCH=CHCH_3$ (XVI). To 17 g of sodium in 250 ml of ether, 41 g of $C_2H_5(CH_3)_2SiCl$ and 1 ml of ethyl acetate were added. Propenyl bromide (47 g) was added in portions. The usual treatment gave 14 g (32.5%) of (XVI), b.p. 114.5-119.5°.

	Found %:	C	65.72;	65.70;	H	12.30;	12.28;	Si	22.37; 22.04
$C_7H_{16}Si$.	Calculated %:	C	65.54;		H	12.57;		Si	21.87

(3-Chloro-2-butenyloxy) trimethylsilane $CH_3C(Cl)=CHCH_2OSi(CH_3)_3$ (XVII).

A mixture of 52 g of $(CH_3)_3SiCl$ and 39 g of 3-chloro-2-buten-1-ol was boiled for four hours until HCl ceased to separate. Distillation through a column gave 33 g (50.8%) of (XVII), b.p. 162-165°.

	Found %:	C	46.54;	46.69;	H	8.08;	8.29		
$C_7H_{15}SiOCl$.	Calculated %:	C	47.00;		H	8.45			

(3-Chloro-2-butenyloxy)triethylsilane $CH_3C(Cl)=CHCH_2OSi(C_2H_5)_3$ (XVIII).

3-Chloro-2-buten-1-ol (109 g) was added to a stirred mixture of 142 g of $(C_2H_5)_3SiCl$, 80 g of pyridine, and 250 ml of benzene. After two days the precipitate of pyridine hydrochloride was filtered off. Fractionation of the filtrate gave 142 g (82.5%) of (XVIII), b.p. 70-72° (2 mm).

	Found %:	C	53.80;	53.85;	H	9.38;	9.36;	Cl	16.33;	16.62;	Si	12.09;	11.5
$C_{10}H_{21}SiOCl$	Calculated %:	C	54.39;		H	9.59;		Cl	16.06;		Si	12.70	

2,2,6,7,7-Pentamethyl-3-oxa-2,7-disilaoct-5-ene $(CH_3)_3SiC(CH_3)=CHCH_2OSi(CH_3)_3$ (XIX).

Reaction was initiated in a mixture of 8 g of sodium, 200 ml of ether, and 21 g of $(CH_3)_3SiCl$ by addition of ethyl acetate, and 28.5 g of (XVII) was then added over a period of two hours. A three-hour boil followed by the usual treatment gave 18 g (52%) of (XIX), b.p. 195°.

	Found %:	C	55.35;	55.42;	H	10.97;	11.14;	Si	25.77;	25.68
$C_{10}H_{24}Si_2O$	Calculated %:	C	55.58;		H	11.11;		Si	25.93	

3,3,8,8-Tetraethyl-7-methyl-4-oxa-3,8-disiladec-6-ene $(C_2H_5)_3SiC(CH_3)=CHCH_2OSi(C_2H_5)_3$ (XX).

To a mixture of 25.5 g of sodium, 500 ml of ether, and 85 g of $(C_2H_5)_3SiCl$, 120 g of (XVIII) was added. The precipitate was filtered off on the next day, and distillation gave 85 g (52%) of (XX), b.p. 101° (2 mm).

	Found %:	C	62.95;	62.90;	H	11.98;	12.12;	Si	18.15;	18.39
$C_{16}H_{36}Si_2O$	Calculated %:	C	63.94;		H	12.04;		Si	18.07	

3-(Trimethylsilyl)-2-buten-1-ol $(CH_3)_3SiC(CH_3)=CHCH_2OH$ (XXI). A mixture of 16 g of (XIX), 20 ml of ethanol, 30 ml of water, and four drops of hydrochloric acid was boiled for eight hours. The product was dried with sodium sulfate and fractionated, when 5 g (60%) of (XXI), b.p. 45-47° (2 mm), was obtained.

	Found %:	C	58.24;	58.28;	H	11.27;	11.11	Si	19.66;	19.54
$C_7H_{16}SiO$	Calculated %:	C	58.30;		H	11.19;		Si	19.42	

3-(Triethylsilyl)-2-buten-1-ol $(C_2H_5)_3SiC(CH_3)=CHCH_2OH$ (XXII). A mixture of 77 g of (XX), 100 ml of ethanol, 23 ml of water, and 3 ml of hydrochloric acid was boiled for three hours. On the next day the mixture was dried and fractionated, when 25 g (59%) of (XXII), b.p. 81° (2 mm), was obtained.

	Found %:	C	63.58;	63.58;	H	11.93;	12.01;	Si	15.78;	15.73
$C_{12}H_{28}SiO$	Calculated %:	C	64.45;		H	11.91;		Si	15.05	

In presence of sodium methoxide, (XXII) combined with acrylonitrile with evolution of heat. The addition product was obtained in 85% yield.

	Found %:	C	65.44;	65.33;	H	10.69;	10.54;	Si	11.69;	11.41
$C_{15}H_{29}SiOH$	Calculated %:	C	65.21;		H	10.52;		Si	11.72	

SUMMARY

1. It was shown that organosilicon compounds having a double bond in the α-position with respect to silicon can be synthesized in high yield by the condensation of chlorotrialkylsilanes with vinyl halide derivatives in ether in presence of sodium activated by ethyl acetate.

2. Silicon tetrachloride was condensed with $CH_2=CHCl$, and R_3SiCl was condensed with $CH_2=CHCl$.

and R_3SiCl was condensed with $CH_3CH{=}CHBr$, $(CH_3)_2C{=}CHBr$, $(CH_3)_2SiCH{=}CHCl$, $(CH_3)_2SiOCl{=}CH_2$ and $R_3SiOCH_2CH{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}Cl$ (R = CH_3 and C_2H_5).

3. Sixteen organosilicon compounds were prepared for the first time. These included tetravinylsilane and 3-(trialkylsilyl)-2-buten-1-ols.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 14. INTERCONVERSION OF 1- AND 2-BUTENES UNDER THE CONDITIONS OF CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

Ya. T. Eidus and R. I. Izmailov

Apart from deuteropropene, the normal butenes are the simplest olefins capable of undergoing isomerization by displacement of the double bond (interconversion of 1- and 2-butenes). These transformations can occur at the actual moment when the butene is formed, e.g. in the dehydration of butanols, the dehydrogenation of butane, the dimerization of ethylene, and other such processes, and also when it is formed intermediately in other reactions.

The interconvension of 1- and 2-butenes is not only of theoretical, but also of practical interest, since in any process one of the isomers may be preferable to the other as starting material [1]. The purely thermal isomerization of the butenes by double-bond displacement occurs at comparatively high temperatures - of the order of 600-650° [2]. A claim made in a patent [3], according to which 1-butene undergoes 87% conversion into 2-butene at 550° in an empty quartz tube, is not very probable since the content of 1-butene in the equilibrium mixture of butenes at this temperature is not more than 35% [4]. At lower temperatures displacement of the double bond can occur only in presence of catalysts. No isomerization of 2-butene into 1-butene was observed at 390°, although cis-trans interconversion proceeded at an appreciable rate [5]. The displacement of the double bond in butenes, occurring in the substances as such or occurring at the moment of their formation, particularly from butanols, has been investigated over various catalysts, of which the most active were found to be, on the one hand, acidic catalysts - sulfuric [6] and phosphoric [6-10] acids, as such or supported on solid carriers, phosphoric oxide [8], aluminum sulfate [7, 8, 11], aluminum phosphate [6], silica gel [7], alumina, apparently when containing acidic impurities [7, 12-15], and natural and synthetic aluminosilicates [16-19] - and, on the other hand, metals and their oxides - ThO_2 [20], Co–Cu–ThO_2 [12], Co on charcoal [21], and metallic nickel [22, 23]. It must be pointed out that reaction over metallic nickel occurs only in the presence of hydrogen [22]. The dimerization of ethylene at 35-40° and 50 atm over cobalt deposited on charcoal yielded a mixture of 1- and 2-butenes, and the relative amount of 1-butene fell as the space velocity of the ethylene was lowered, which indicates that the 1-butene formed initially was isomerized into 2-butene. Over the catalyst Co–Cu–ThO_2, which is active in the synthesis of hydrocarbons from carbon monoxide and hydrogen, the treatment of 1-butene at 190° and atmospheric pressure gave a gas containing 34% of 2-butene [12]. When the reaction products were again passed over the catalyst, the outgoing gas already contained 53% of 2-butene. In a similar experiment with cis-2-butene, the outgoing gas contained 7% of 1-butene. In experiments lasting 20-24 hours in a circulating system, equilibrium was attained when the original gas was cis-2-butene or a mixture containing 13.8% of 1-butene. The equilibrium mixture contained 11.3% of 1-butene, 31.0% of cis-2-butene, and 57.7% of trans-2-butene; no isobutene was formed. However, over a catalyst that had not been regenerated practically no displacement of the double bond occurred.

The present investigation had the object of determining the possibility of the isomerization of 1-butene into 2-butene, and of the reverse reaction, under the conditions required for the catalytic hydrocondensation of carbon monoxide with olefins [24]. This question has a direct bearing on a previous investigation on the hydrocondensation of carbon monoxide with butene obtained by the dehydration of 1-butanol over alumina at

400° [25] and also on the view that the formation of hydrocarbon chains in the hydrocondensation of carbon monoxide with ethylene and propene proceeds stepwise, and therefore with the intermediate formation of butene. In order to resolve this question, an investigation was made of the behavior of 1- and 2-butenes over a catalyst for the reaction of hydrocondensation at atmospheric pressure and 190° in absence and in presence of hydrogen, but always in absence of carbon monoxide.

EXPERIMENTAL

The determination of the composition of the mixture of butenes was one of the most complicated tasks arising in the investigation of the isomerization of butenes. Analytical errors give rise to numerous discrepancies between the results obtained by different authors. Various methods based on the bromination of the mixture of butenes, which have been used previously [6, 13, 17], were found to be inaccurate owing to the possibility of the thermal isomerization of the dibromides during fractionation. Low-temperature fractionation of butenes through a Podbielniak column [6, 7, 12, 15], supplemented by the usual gas analysis of the fractions [7, 12], is also inadequate. A simple, rapid method of determining the composition of a liquid mixture of normal butenes is the measurement of its vapor pressure at −80° [22] or 0° [26].

We used a combined method for the determination of mixtures of butenes; it included low-temperature fractionation through a Podbielniak column, sulfuric acid analysis of the fractions supplemented by a test for isobutene with the Deniges reagent, and determination of the vapor pressures of the liquefied fractions at 0°. In calculating the composition of mixtures from vapor pressures we used Raoult's law. The linearity of the relationship between vapor pressure and molar composition has been shown previously [19]. The probable error in the method based on vapor pressure at 0° is less than 1%. Vapor pressures at 0° P_0 are as follows [26]: isobutene 988.4 ± 0.6 mm, 1-butene 964 ± 1 mm, trans-2-butene 733.6 ± 0.3 mm, cis-2-butene 660 ± 1.5 mm, and butane 775 mm [27].

Preparation of 1-Butene

Freshly prepared butyl alcohol - b.p. 116.5-117.0° (756 mm), n_D^{20} 1.3991, d_4^{20} 0.8098; found MR 22.13; calculated for C_4H_9OH MR 22.20 (the literature [28, 29] gives n_D^{20} 1.3992, d_4^{20} 0.80978) - was dehydrated over commercial alumina at 390°. The resulting gas was dried over calcium chloride and frozen out with a mixture of solid carbon dioxide and acetone. In order to enrich it in 1-butene, the liquid butene was fractionated through a Podbielniak low-temperature column, the distillate being collected from −6.2° upwards. The result of such a fractionation (23 ml of liquid butene) is given in Table 1.

TABLE 1

Fraction	Boiling limits (°C)	Yield of fraction (liters of gas)	Vapor pressure at 0° P_0 (mm)	1-Butene content (%)	2-Butene content (%)
I*	From −6.2 to −6 (inclusive)	5.4	952	95.5	4.5
II	From −6 to +0.8	1.0	880	55.5	44.5
III	From +0.8 to +3	0.65	782	21.3	78.7

Refractionation of Fraction I through the same column gave a narrow fraction of b.p. −6° and P_0 962.5 mm, which corresponds to 92.4% of 1-butene and 0.6% of 2-butene; it comprised about 60% of Fraction I and about 45% of the original butene. In other batches treated in this way we succeeded in obtaining 1-butene having P_0 964 mm.

* Fraction I contained about 0.4% of isobutene.

Preparation of 2-Butene

2-Butene was prepared from 2-butanol by dehydration over alumina at 340°. The 2-butanol was prepared by the hydrogenation of 2-butanone, and it was distilled through a 40-plate column before use; it then had b.p. 99.2° (758 mm), n_D^{20} 1.3970, d_4^{20} 0.8068, found MR 22.11; calculated for C_4H_9OH MR 22.20 (the literature [30] gives n_D^{20} 1.39780, [31] 1.3973 [32], d_4^{20} 0.8063 [29], 0.80652 [33], b.p. 99.5° (760 mm), [34] 99.53°). The butene so obtained contained 99% of normal butenes and about 1% of isobutene; when liquefied it had P_0 775 mm.

The liquid butene (175 ml) was fractionated through the low-temperature column, and 6 liters of gas (13.7%) came over from −42° to +0.8° (up to −4°, 2.5 liters came over; from −4° to −1°, 1.5 liters; from −1° to +0.2°, 1 liter; and from +0.2° to +0.8°, 1 liter). This fraction (b.p. from −42° to +0.8°) had P_0 1050 mm. The whole of the residue (86.3%) was fractionated through the same column over the range 0.8-4° into five different fractions, each consisting of 30 ml of liquid, and having P_0 = 748, 743, 732.8, 729.8, and 728 mm respectively. The last fraction (P_0 = 731 mm), which contained neither 1-butene nor isobutene, was taken for the experiments.

In all of the experiments the catalysts (30 ml each) were taken from the same preparation; before use they were treated with hydrogen at 450°. Their activity in the reaction of hydrocondensation of carbon monoxide with olefins, which was tested with a gas mixture consisting of 70% C_2H_4, 5% CO, and 25% H_2 at 190° and at a space velocity of 100 hour^{-1}, may be expressed by the yield of hydrocarbons, which was about 500 ml per cu.m. After the isomerization experiments the catalysts preserved their activity for the hydrocondensation reaction. The experiments were carried out in a glass tube 12 mm in diameter.

1) In Absence of Hydrogen (Experiment 287, Catalyst 64). In order to remove hydrogen completely from the surface of the catalyst, nitrogen was displaced at 190°, and 1-butene (P_0 964 mm) was passed for two hours at a space velocity of 70 hour^{-1}. The volume passed was 4200 ml, and 2800 ml of gas was recovered having P_0 924 mm and a composition of 98.6% n-C_4H_8 and 1.4% C_4H_{10}, which corresponds to 83.3% of 1-butene, 15.3% of 2-butene, and 1.4% of butane*. Under the same conditions a further 2630 ml of the same 1-butene was passed, and 2600 ml of gas was recovered having P_0 953 mm and a composition of 100% of n-butene; finally a further 2100 ml of 1-butene was passed and 2100 ml of gas was recovered having P_0 953 mm and a composition of 100% of n-butene. Both of the last two portions of gas obtained by passage of 1-butene over the catalyst had the composition of 95.8% of 1-butene and 4.2% of 2-butene**. Thus, in absence of hydrogen 1-butene undergoes very little isomerization (about 4%); when hydrogen is present in the catalyst but not in the original gas, 1-butene isomerizes to the extent of about 15%.

2) In Presence of Hydrogen (Experiment 288, Catalyst 65). A gaseous mixture consisting of 90.1% of 1-butene (P_0 962.5 mm, corresponding to 0.6% of 2-butene) and 9.9% of hydrogen was passed at 190° over Catalyst 65 at a space velocity of 66 hour^{-1}. The volume passed was 7700 ml, including 6900 ml of butene and 760 ml of hydrogen. The outgoing gas was frozen out at −70°, 225 ml of gas not being condensed at this temperature (8.2% C_2H_4 + 91.8% H_2 + CH_4 + C_2H_6). About 15 ml of liquid was condensed, and on evaporation this gave 3700 ml of gas of composition 0.4% of isobutene, 90.5% C_nH_{2n} and 9.1% C_nH_{2n+2}. The condensate was fractionated through a Podbielniak column, and the part boiling below the butenes (from −105° to −30°), which comprised 4.4% of the condensate, had the composition 16.5% C_2H_4, 22.0% C_3H_6, and 61.5% C_nH_{2n+2} ($n < 4$). The fractionation curve for this part of the condensate is shown in Fig. 1.

From the curve in Fig. 1 it can be calculated that $C_2H_4 : C_2H_6 : C_3H_6 = 1.0 : 1.1 : 1.5$. The second row of figures along the axis of abscissae in Fig. 1 give the percentage of the whole condensate. The remaining 95.6% of the condensate formed the C_4 fraction and had the following composition: 0.4% of isobutene, 90.9%

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* Calculated for the formation of an equilibrium mixture of cis- and trans-2-butenes. When calculated for trans-2-butene, 16.2% of 2-butene is obtained instead of 15.3%.

** Calculated for an equilibrium mixture of the two forms of 2-butene; when calculated for trans-2-butene a composition of 95.8% of 1-butene and 4.2% of 2-butene is obtained.

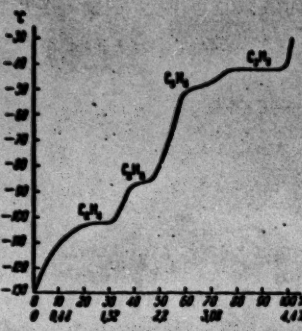

Fig. 1. Fractionation curve for products boiling below the butenes formed in the isomerization of 1-butene (Experiment 288)

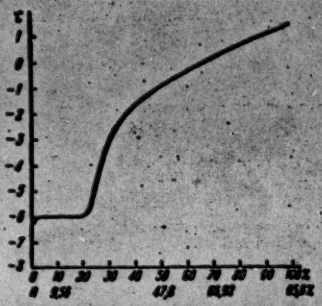

Fig. 2. Fractionation curve for the C_4 fraction of products formed in the isomerization of 1-butene (Experiment 288)

of n-butenes, and 8.7% of butane. The C_4 fraction of the reaction product was fractionated through the same column. The results of the fractionation are give in Table 2. The contents of 1- and 2-butenes were calculated from the vapor pressures P_0, taking into account the contents of butane, isobutene, and n-butenes found by gas analysis.

TABLE 2

Fraction	Boiling limits (°C)	Yield of fraction (% on original C_4 fraction)	Vapor pressure at 0° P_0 (mm)	1-Butene content		2-Butene content		Isobutene content		Butane content	
				(%)	(ml of gas)	(%)	(ml of gas)	(%)	(ml of gas)	(%)	(ml of gas)
I	−6	26	970	97	883	–	–	0.6	5.5	2.4	22
II	From −6 to −0.7	28	877	59.4	582	23.2	227	–	–	17.4	171
III	From −0.7 to +3	46	725	–	–	89.1	1434	–	–	10.9	176

The fractionation curve for the C_4 fraction is shown in Fig. 2. No residue corresponding to C_5 hydrocarbons and hydrocarbons of still higher-boiling point was obtained.

It follows from Table 2 that the C_4 fraction of the product of the isomerization of 1-butene in presence of 10% of hydrogen had the following composition: 41.9% of 1-butene, 47.5% of 2-butene, 10.4% of butane, and 0.2% of isobutene. From the data on the composition and P_0 of Fraction III, which contained the bulk of the 2-butene (86%), it was found that the relative amounts of cis- and trans-2-butenes in this fraction was 1 : 4.3.

Hence, the isomeric transformation of 1-butene into 2-butene occurs at 190° in presence of 10% of hydrogen. At a space velocity of 66 $hour^{-1}$ a mixture was obtained in which the relative amounts of 1- and 2-butenes were 1 : 1.1, the equilibrium ratio at 190° being 10.8 : 89.2 [4]. The relative amounts of cis- and trans-2-butenes were 1 : 5.1 (equilibrium ratio 29.5 : 59.7 [4]). In the course of the reaction partial hydrogenation occurred. The C_4 fraction contained 10.4% of butane. Hydrogenolysis and skeletal isomerization of 1-butene occurred to a negligible extent.

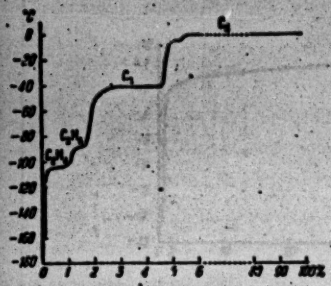

Fig. 3. Fractionation curve for products obtained in the isomerization of 2-butene (Experiment 291)

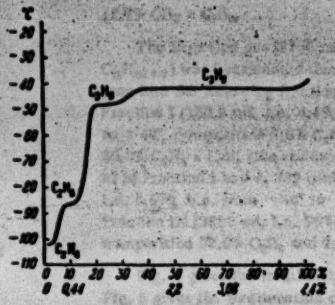

Fig. 4. Fractionation curve for products boiling below the butenes formed in the isomerization of 2-butene (Experiment 292)

Experiments on the Isomerization of 2-Butene into 1-Butene

1) In Absence of Hydrogen (Experiment 289, Catalyst 66). Hydrogen was displaced from the reaction tube with nitrogen at 250°, and then 2-butene was passed at 190° with the result that some hydrogenation occurred [the outgoing gas (600 ml) contained 82.7% of butene and 17.3% of butane]. More 2-butene (P_0 731 mm, 96.5% trans and 3.5% cis) was then passed over the catalyst at 190° at a space velocity of 66 hour^{-1}. The volume of gaseous 2-butene that was passed was 3500 ml, and this was recovered almost without change in volume; it contained 100% of 2-butene and after liquefaction had P_0 731.5 mm. Under these conditions, therefore, 2-butene is not isomerized into 1-butene and does not undergo cis-trans isomerization.

Experiment 290. 2-Butene (3700 ml, P_0 731 mm) was passed over the same catalyst at the same space velocity at 230°. The outgoing gas had P_0 739.5 mm after liquefaction and contained 0.7% of isobutene and 99.3% of n-butenes. These results correspond to a 1-butene content of 2.9%. Hence, even at a higher temperature (230°) the extent to which double-bond displacement occurs in 2-butene is very small.

2) In Presence of Hydrogen (Experiment 291, Catalyst 67). A gaseous mixture (7200 ml) of 90% 2-butene (P_0 728 mm, 6.8% cis and 93.2% trans) and 10% hydrogen was passed over the catalyst at 190° and at a space velocity of 69 hour^{-1}. The volume of gas recovered was 3600 ml, the liquefaction of which gave 15 ml of liquid having P_0 881.5 mm and composition: 0.3% of isobutene, 93.2% C_nH_{2n}, and 6.5% C_nH_{2n+2}. This 15 ml was fractionated through a Podbielniak column with the following results: driven off up to −40°, 153 ml of gas (Fraction I), which formed 4.6% of the whole and had the composition 15.2% C_2H_6, 34.9% C_3H_8, and 49.9% C_nH_{2n+2}. The residue (P_0 729.5 mm) was fractionated into two fractions: Fraction II (23 ml of gas), b.p. from −7° to −5°, and Fraction III (3330 ml of gas), b.p. 0-3°. Fraction III did not contain isobutene and consisted of 95.5% of n-butenes and 4.5% of butane. It follows from these data that the overall composition of the condensed gas was 0.75% of ethylene, 1.6% of propene, 4.2% of butane, 90.4% of 2-butene, 2.25% of ethane + propane, and 0.7% of 1-butene + isobutene.

In Experiment 291 not only gas, but also 0.3 ml of liquid condensable at room temperature was obtained, this representing a yield of liquid hydrocarbons of 37.5 ml per cu.m.

Hence, in the study of the displacement of the double bond in 2-butene in presence of 10% of hydrogen at 190°, practically no 1-butene was detected in the reaction products. Partial hydrogenation and hydrogenolysis occurred and, to a very slight extent, also hydropolymerization.

Experiment 292. An isomerization experiment was carried out with the same Catalyst 67 on a mixture of 73.4% of 2-butene (P_0 728 mm) and 26.6% of hydrogen at 190° and a space velocity of 100 hour^{-1}. The volume of gaseous mixture passed was 9000 ml, and the products were 0.5 ml of liquid condensate (50 ml per cu.m), 3750 ml of gas, which condensed to 15 ml of liquid, and 900 ml of gas, which did not condense at −70°

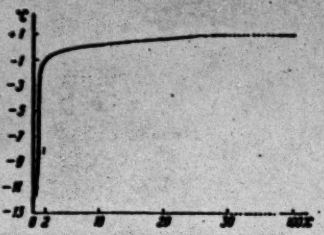

Fig. 5. Fractionation curve for the C_4 fraction from 2-butene (Experiment 292)

and had the composition: 7.2% C_2H_6, 80.1% H_2, and 12.7% $CH_4 + C_2H_6$.

The liquefied gas (3750 ml, 89.0% C_nH_{2n}; 11.0% C_nH_{2n+2}) was fractionated through a Podbielniak column into the following fractions (Figures 4 and 5): Fraction I (163.8 ml, i.e. 4.4% of gas), b.p. from −105° to −40°, composition 7.8% C_3H_6, 29.2% C_3H_8, and 63.0% $C_3H_6 + C_3H_8$ (the residue remaining after removal of Fraction I had P_0 739 mm); Fraction II (23.4 ml, i.e. 0.6%), b.p. from −40° to −2° (not analyzed); and Fraction III (3557 ml, i.e. 95%), b.p. from −2° to +1°, composition 92.0% C_4H_8 and 7.4% C_4H_{10}.

Fig. 4 gives the fractionation curve for Fraction I, Fig. 5 gives the fractionation curve for Fractions II and III.

The condensed gas had the following composition: 0.3% C_2H_6, 1.3% C_3H_6, 0.6% of 1-butene (in admixture with isobutene), 88.0% of 2-butene, 2.8% of $C_2H_6 + C_3H_8$, and 7% of C_4H_{10}. It will be seen from these results that 1-butene is practically absent from the outgoing gas.

TABLE 3

Original gas		Space velocity ($hour^{-1}$)	Composition of C_4 fraction of reaction product (%)			
Butene	Hydrogen (%)		1-Butene	2-Butene	Butane	1-Butene / 2-Butene
1-Butene	0	70	95.8	4.2	—	1 : 0.04
1-Butene	9.9	66	41.9	47.5	10.4	1 : 1.1
2-Butene	0	66	—	100	—	—
2-Butene	10	69	0.7	94.9	4.4	1 : 174
2-Butene	26.6	100	0.7	92.0	7.3	1 : 171

Table 3 gives a general summary of the results obtained on the isomerization of 1-butene into 2-butene and vice versa over a hydrocondensation catalyst at 190°.

It is notable that 1-butene is isomerized into 2-butene in presence of hydrogen, a fact that proves the activity of the catalyst for this reaction. A considerable proportion of the 1-butene remains adsorbed on the catalyst surface; when the initial gas consists entirely of olefin (hydrogen absent), the extent to which it is absorbed is less. It appears that, in presence of hydrogen, 2-butene is isomerized into 1-butene, but this remains adsorbed on the catalyst surface.

SUMMARY

1. The catalytic reaction 1-butene ⇌ 2-butene was studied both in presence and in absence of hydrogen, the conditions being those for the hydrocondensation of carbon monoxide with olefins, carbon monoxide, however, being absent.

2. It was shown that, in absence of hydrogen, the isomerization of 1-butene into 2-butene and vice versa did not occur to an appreciable extent.

3. In presence of 10% of hydrogen, 1-butene was isomerized into 2-butene, the relative amounts of 1- and 2-butenes in the products being 1 : 1.1 (at a space velocity of 66 $hour^{-1}$).

4. In experiments on the isomerization of 2-butenes in presence of 10% and 26.6% of hydrogen at space velocities of 69 and 100 $hour^{-1}$, no appreciable amount of 1-butene could be detected in the reaction product.

5. In experiments with 1-butene, hydrogenation of the olefin proceeded much more rapidly (about twice as fast) than in experiments with 2-butene under similar conditions.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 15. HYDROCONDENSATION OF CARBON MONOXIDE WITH 2-BUTENE

Ya. T. Eidus and R. I. Izmailov.

In a previous communication [1] we described experiments on the hydrocondensation of carbon monoxide with the butene obtained by dehydration of butyl alcohol over alumina, which consists of a mixture of 1- and 2-butenes, the former predominating. We used an equimolecular mixture of the butene obtained in this way and hydrogen, and 4-6% of carbon monoxide was added. The hydrocondensation reaction gave liquid hydrocarbons in a yield of 635 ml per cu.m, or 55 ml per liter of catalyst per hour. About 30-35% of the olefin that reacted was hydrogenated to butane. After being "debutanized", the liquid condensate boiled over the range 28-276° and contained 28% of olefins; after hydrogenation the following fractions were found (% by volume): about 24% of the C_5 fraction (about half of this was isopentane), 15% of the C_6 fraction, 8% each of the C_7 and C_8 fractions, and 9% of the C_9 fraction.

It was of interest to investigate the behavior of 2-butene in the reaction of hydrocondensation with carbon monoxide, for there were no data on the behavior of symmetrically disubstituted ethylenes in this reaction. When an attempt was made to use cyclohexene - which can be regarded as a symmetrically disubstituted ethylene - in the reaction of hydrocondensation with carbon monoxide [2], it was found that "irreversible" catalysis and hydrogenation to cyclohexane occurred, but methylation with formation of methyl- and 1,2-dimethylcyclohexenes occurred only to a slight extent.

The object of the present investigation was the study of the hydrocondensation of carbon monoxide with 2-butene. The apparatus and experimental procedure were the same as in previous work [1]. The preparation of pure 2-butene for use as a component of the initial gas mixtures and the method of determining the composition of the C_4 fraction were described in the preceding paper [3]. All of the catalysts were samples from the same preparation.

EXPERIMENTAL

Table 1 gives details of experiments on the hydrocondensation of carbon monoxide with 2-butene at 190° and atmospheric pressure in a continuous-flow system. The glass reaction tube was 12 mm in diameter. Catalysts 68-72 were used (30 ml of each, except Catalyst 71, of which 50 ml was taken), and these were regenerated after every 15 hours. The ingoing mixture was prepared from 2-butene that contained no 1-butene or isobutene as impurity and had a vapor pressure at 0° (P_0) of 728-732 mm, which corresponds to trans-2-butene in admixture with 2.2-7.6% of cis-2-butene. The mixture consisted of 70-75% of 2-butene, 21-26% of hydrogen, and 4-6% of carbon monoxide.

The gas was passed over the catalyst at a space velocity of 100 $hour^{-1}$. As can be seen from Table 1, the yield of liquid hydrocarbons calculated on $C_4H_8 + H_2 + CO$ was 350-550 ml per cu.m or 32-55 ml per liter of catalyst per hour, the contraction in the gas being 33-39.5%. The ratio of heavy oil to light was 1.2 : 3.2.

TABLE 1

Catalyst	Experiment	Duration of expt. (hour)	Space velocity (hour^{-1})	Contraction	Composition original gas (% by vol)			Yield (ml/cu.m)			Yield of H + L (ml/liter.hour)
					2-Butene	H_2	CO	Heavy oil (H)	Light oil (L)	H + L	
68	293	6.5	91	35.0	72.7	22.6	4.7	254.2	101.7	355.9	32.3
68	294	6.5	100	35.7	74.4	21.2	4.4	204.1	173.5	377.5	37.9
69	295	12.0	99	37.3	72.2	23.1	4.7	275.7	192.1	267.8	45.8
69	296	13.0	101	37.0	71.5	23.0	5.5	309.8	232.5	542.3	55.5
70	297	13.0	100	33 0	71.3	23.3	5.4	209.3	92.0	301.3	30.2
71	298	11.0	103	38.5	72.0	22.1	5.9	264.5	87.3	351.8	36.0
72	299	12.5	102	39.5	72.6	23.0	4.4	240.4	108.5	348.9	35.8
72	300	23.2	102	33.3	70.0	26.0	4.0	243.1	101.5	344.6	35.2
72	301	40.0	100	34.3	70.7	24.2	5.1	219.8	185.3	405.1	40.5

TABLE 2

Fraction	B.p. (°C)	Content of fraction in outgoing gas	Composition of fraction		
			Gas	(% on fraction)	(% on outgoing gas)
I	−160 to −110	26.0	H_2	63.0	16.4
			CO	14.6	3.8
			CH_4	22.4	5.8
II	−110 to −10	4.5	C_2H_4	2.8	0.13
			C_2H_6	17.8	0.8
			$C_3H_6+C_3H_8$	74.0	3.33
			CO	5.4	0.24
III	−10 to 2	69.5	2-Butene	95.5	66.4
			Butane	4.5	3.14

In some experiments the composition of the outgoing gas was determined, and on the basis of the results obtained the extent to which each component of the original mixture took part in the reaction was determined. As an example we will cite the results obtained in Experiment 294 (Table 1). In this experiment we passed 19600 ml of gas (STP) of the composition shown in Table 1 and, apart from liquid condensate, we obtained 11600 ml of gas, of which 2700 ml did not condense and 8900 ml did condense at −70°. Part (3000 ml) of the gas obtained was fractionated through a Podbielniak low-temperature column. The results of the fractionation are shown in Table 1 and Fig. 1.

Fraction III had P_0 732 mm and contained neither 1-butene nor isobutene. The original 2-butene had P_0 731 mm, corresponding to trans-2-butene in admixture with 3.4% of cis-2-butene. Fraction III contained 4.8% of cis-2-butene. Analysis of the results given in Table 2 showed that 2-butene reacted to the extent of 47.2%, hydrogen to the extent of 54.3%, and carbon monoxide to the extent of 45.8%. The products of hydrocracking ($C_1 + C_2 + C_3$) corresponded to about 2% of the original 2-butene and about 4% of the 2-butene that reacted; the corresponding figures for butane were 2.5% and 5.0% approximately.

The liquid condensate (about 170 ml) obtained in Experiments 293-301 was separated from water formed in the reaction, washed twice with 2% caustic soda, washed with water until neutral, and sealed in a tube over anhydrous copper sulfate. After being dehydrated, the condensate was filtered from copper sulfate and "debutanized" in a low-temperature column, about 18% by volume of the condensate being distilled off below 20°; the

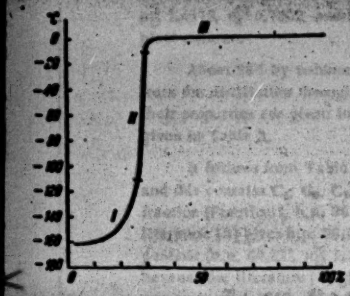


Fig. 1. Fractionation curve for the gaseous fraction of the products of the hydrocondensation of carbon monoxide with 2-butene

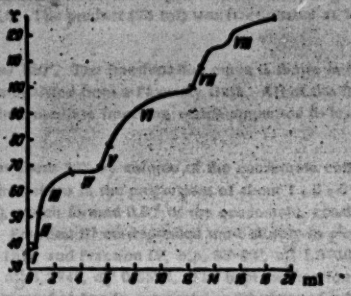


Fig. 2. Fractionation curve for liquid hydrocarbons obtained in the hydrocondensation of carbon monoxide with 2-butene

TABLE 3

Fraction	B.p. (°C)	Content of fraction in original condensate	n_D^{20}	d_4^{20}	C_n
I	30—38	0.8	1.3579	—	C_5
II	45—51	0.4	1.3620	—	C_5
III	53—68	3.4	1.3718	0.6494	C_5
IV	68—69	2.7	1.3750	0.6580	C_5
V	72—78	1.4	1.3771	0.6616	C_5
VI	80—100	8.4	1.3859	0.6806	C_5
VII	104—108	1.4	1.3897	0.6801	C_5
VIII	110—127	7.5	1.3967	0.7013	C_6
IX	128—152	3.8	1.4056	0.7178	C_6
X	158—174	4.8	1.4096	0.7272	C_6
XI	180—200	5.3	1.4163	0.7415	C_6
XII	215—220	3.4	1.4241	0.7556	C_6
XIII	226—241	5.2	1.4273	0.7665	C_6
XIV	247—260	4.8	1.4323	0.7709	C_6
XV	268—280	6.9	1.4362	0.7784	C_{12}
XVI	288—310	6.6	1.4400	0.7856	C_{12}, C_{17}
XVII	316—332	9.6	—	0.8019	C_{18}
Residue	—	11.0	—	—	—
Original condensate	—	—	1.4179	0.7382	—

distillate contained 85.8% of 2-butene and 14.2% of butane. These amounts of 2-butene and butane, which must be taken into account in the investigation of the outgoing gas, are so small that they do not introduce any substantial changes in the composition as calculated above. After being debutanized the condensate had n_D^{20} 1.4215 and d_4^{20} 0.7389; the refractive index did not change when the condensate was boiled over sodium for two hours under a short low-temperature column.

The debutanized condensate (90 ml; bromine value 38.9, corresponding to about 37% of unsaturated hydrocarbons) was hydrogenated in presence of platinized charcoal (3 ml) to which H_2PtCl_6 had been added [4].

After the absorption of 3500 ml (STP) of hydrogen, a further 1 ml of platinized charcoal was added and a further 100 ml of hydrogen was then absorbed. After being dried over copper sulfate the hydrogenation product had n_D^{20} 1.4178, d_4^{20} 0.7362, and bromine value 0.6. The product (73 ml) was fractionated at 747 mm through a 40-plate column.

About 26% by volume came over below 130°. The fractionation curve is shown in Fig. 2. The residue from the distillation through the column was distilled from a Favorsky flask. All of the fractions collected and their properties are given in Table 3. The intermediate fractions, which amounted to less than 0.3% are not given in Table 3.

It follows from Table 3 and Fig. 2 that about 30% by volume of the condensate comes over below 153°, and this contains C_5, C_6, C_7, C_8, and C_9 hydrocarbons in the proportions of about 1 : 6 : 9 : 8 : 4. The pentane fraction (Fraction I, b.p. 36-38°, n_D^{20} 1.3579), which formed 0.8% of the condensate, consisted of n-pentane (the literature [5] gives b.p. 36.07°, n_D^{20} 1.3575). Fraction III corresponded most closely in properties to 2-methylpentane (b.p. 60.27°, n_D^{20} 1.3715, d_4^{20} 0.6532 [5]), and Fraction IV, b.p. 68-69°, n_D^{20} 1.3750, d_4^{20} 0.6580, was n-hexane (the literature [5] gives b.p. 68.74°, n_D^{20} 1.3749, d_4^{20} 0.6594. The heptane fraction (Fraction VI) had the constants n_D^{20} 1.3859, d_4^{20} 0.6806, which are somewhat low in comparison with those of n-heptane (b.p. 98.43°, n_D^{20} 1.3877, d_4^{20} 0.6837 [5]).

Of the heptane isomers having one side chain only 2-methylhexane has lower constants (b.p. 90.05°, n_D^{20} 1.3849, d_4^{20} 0.6786 [5]) than n-heptane, and we may therefore assume that Fraction VI contains some of this hydrocarbon. Fraction VIII, b.p. 110-127°, n_D^{20} 1.3967, d_4^{20} 0.7013, is close in properties to n-octane (b.p. 125.67°, n_D^{20} 1.3974, d_4^{20} 0.7025 [5]), but its constants are somewhat low. In this case only 2-methylheptane (b.p. 117.65°, n_D^{20} 1.3950, d_4^{20} 0.6979 [5]) has lower constants than n-octane, and it may be assumed that it is present in Fraction VIII. This is confirmed also by the presence on the fractionation curve (Fig. 2) of a step corresponding to n-octane. We are not here taking account of more highly branched hydrocarbons because their formation is not very likely under the conditions of reaction.

When Fractions VIII and VI and a mixture of Fractions III and IV were investigated by the Raman-spectrum method*, only C_5, C_7, and C_8 n-alkanes were detected, the corresponding characteristic wave numbers (cm^{-1}) being: Fraction VIII - 813, 860, 878, 895, 1030, 1044, 1062, 1085, 1140, 1304, 1440, 1460; Fraction VI - 310, 836, 852, 905, 1080, 1140, 1305, 1440, 1460; mixture of Fractions III and IV - 826, 893, 901, 1040, 1140 [1].

It will be clear from these results that the hydrocondensate obtained from carbon monoxide and 2-butene consists essentially of normal alkanes, probably together with a small amount of 2-methylalkanes. The results show that 2-butene itself participates only to an insignificant extent in the hydrocondensation reaction, the reaction products being mainly formed from a 1-alkene, i.e. from 1-butene, which is doubtless formed by the catalytic isomerization of 2-butene.

In the preceding paper [3] we studied the catalytic isomerization of 2-butene into 1-butene and of 1-butene into 2-butene under the conditions of the hydrocondensation of carbon monoxide with olefins, both in presence and in absence of hydrogen, but always in absence of carbon monoxide. It was shown that the hydrocondensation catalyst is active in the reaction of double-bond displacement only when hydrogen is present. 1-butene in admixture with 10% of hydrogen being partially isomerized into 2-butene with formation of an approximately equimolecular mixture of 1-butene and 2-butene. On the other hand, in experiments with 2-butene passed in admixture with 10 or 26% of hydrogen over the hydrocondensation catalyst under the same conditions, no 1-butene was found in the outgoing gas, in spite of the fact that there should be about 10% present in an equilibrium mixture. In the isomerization experiments, both on 1-butene and on 2-butene, a considerable proportion of the olefin remained adsorbed on the catalyst surface and some of it was hydrogenated to butane (somewhat more in the 1-butene experiments than in those on 2-butene).

The results obtained in the present investigation show quite clearly that, under hydrocondensation conditions, isomerization of 2-butene into 1-butene does occur, but the 1-butene formed (calculation shows that not more than 5-6% can be formed) remains adsorbed on the catalyst surface and then, when it becomes possible to

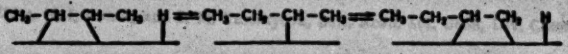
* The spectra were determined by Yu. P. Egorov, to whom we express our thanks.

enter into the reaction of hydrocondensation with carbon monoxide, is converted into high-boiling products; the 2-butene continues to isomerize into 1-butene.

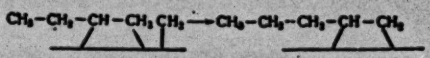
Hence, the products of the hydrocondensation of 2-butene with carbon monoxide are really formed from the 1-butene produced by displacement of the double bond of 2-butene. It is interesting that the whole of the 1-butene formed in this way takes part in the hydrocondensation reaction, for, as we saw above, only 2-butene is present in the outgoing gas.

The formation of some of the products of the hydrocondensation of carbon monoxide with 2-butene can be expressed schematically as follows.

1) Isomerization of 2-butene into 1-butene [8]:

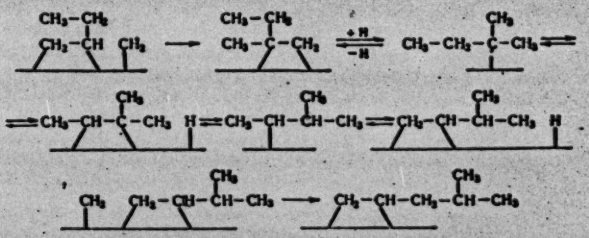


2) Formation of pentene:



In a previous investigation [7] 5.5-7% of a C_6 fraction was obtained in the hydrocondensation of 1-hexene with carbon monoxide, and this could be formed only by the hydrocracking of the original 1-hexene and its transformation products. In experiments with 2-butene in the present investigation, hydrocracking products (about 4%) boiling lower than the butenes were again obtained. It is probable that olefins containing five or more carbon atoms can also be formed to some extent by the hydrocracking of hydrocarbons of higher molecular weight formed in the reaction.

3) The formation of 2-methylpentane, 2-methylhexane, and 2-methylheptane, which appear to be formed in small amounts, can be represented as follows, the starting substance being 1-butene [8]:



Hydrogenation of the adsorbed isomeric methylpentenes give 2-methylpentane. 2-Methylhexane and 2-methylheptane can be formed from methylpentene by analogous reactions, and these may arise also by the polymerization and copolymerization of olefins formed by hydrocracking.

4) Formation of octene by dimerization [8]:

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CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE BY OXIDIZING AGENTS

COMMUNICATION 10. OXIDATION OF HYDROXY COMPOUNDS OF LOW MOLECULAR WEIGHT WITH NITROGEN DIOXIDE

E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova

In the literature the view is widely held that, in the cold, nitrogen dioxide is a specific oxidant for carbohydrates, in which it attacks primary alcohol groups, but has no effect on secondary alcohol groups. On the basis of this hypothesis, nitrogen dioxide has been used for the preparation of glucosiduronic acids from glucosides [1] in 75-80% yield and dicarboxylic acids from monosaccharides in 44% yield [2]. On the basis of the same hypothesis, Kenyon has stated that cellulose oxidzed with nitrogen dioxide is a "celluronic acid", i.e., that the C-6 primary alcohol groups of the glucose residues are oxidized to carboxyl groups and no other oxidative changes occur [3].

Doubt has been thrown on the correctness of this assertion by us, by Nevell [4], and by Nabar and Padmanabhan [5]. According to our work [6], in the preparation of oxycelluloses by NO_2 oxidation, not only are the primary alcohol groups oxidized, but also the secondary alcohol groups, which are converted into keto groups. It was therefore of interest to obtain a more precise idea of the course of the oxidative reactions occurring when nitrogen dioxide reacts with various hydroxy compounds of low molecular weight. For this purpose we selected isopropyl alcohol, ethylene glycol, 1,2-propanediol, and methyl glucoside.

EXPERIMENTAL

The hydroxy compounds were oxidized with nitrogen dioxide in carbon tetrachloride solution at not above 20°, the medium either being anhydrous or having an addition of 5% of water on the weight of hydroxy compound so that the effect of water on the course of the reaction could be determined. The amount of nitrogen dioxide (distilled over phosphoric oxide and oxidized to completion in a current of oxygen; b.p. 21.2-21.5°) brought into reaction was 50% of the amount calculated for the complete oxidation of all primary alcohol groups to carboxyls and all secondary alcohol groups to keto groups. The hydroxy compounds were dried and distilled before reaction. Isopropyl alcohol boiled at 82.1° and contained 0.1% of acetone; ethylene glycol had b.p. 195°, n_D^{20} 1.4319; 1,2-propanediol had b.p. 104° (30 mm), n_D^{20} 1.4330; methyl glucoside melted at 166°.

The reaction was carried out in a three-necked flask fitted with condenser, stirrer, and dropping funnel. A weighed amount (0.2-0.5 mole) of the hydroxy compound, contained in 50 ml of carbon tetrachloride, was introduced into the flask, and a solution of the required amount of nitrogen dioxide in 50 ml of carbon tetrachloride was added through the dropping funnel. Heat was evolved, and the mixture was cooled so that the temperature did not rise above 20°. The reaction mixture was stirred for 1-2 hours, and then set aside at room temperature for 20 hours. Oily drops generally floated on the top of the greenish-yellow solution. After 20-24 hours the reaction was brought to an end, the excess of nitrogen oxides being removed in the cold under reduced pressure. The solution was poured into water, the liquid layers were separated, and the carbon tetrachloride layer was washed several times with water. The aqueous and carbon tetrachloride layers were investigated separately.

TABLE 1
Summary of Oxidation Experiments

Experiment No.	Composition of reaction mixture (moles)	Experimental conditions	Water-soluble fraction		Total yield from aqueous fraction and hydrolyzed CCl_4 fraction (%)
			Carbonyl compounds (mg-equiv)	Acids (mg-equiv)	
1	Isopropyl alcohol 0.52, NO_2 0.26	26°, 25 hours	Acetone 11.5	Formic acid 0.2, acetic acid	Acetone 4.7
2	Isopropyl alcohol 0.52, NO_2 0.26, H_2O 0.08	26°, 25 hours	Acetone 29.6	Formic acid 0.16, acetic acid	Acetone 12
3	Ethylene glycol 0.25, NO_2 0.50	14°, 24 hours	Glycolaldehyde traces	Glycolic acid present, oxalic acid traces	–
4	Ethylene glycol 0.25, NO_2 0.50, H_2O 0.05	14°, 24 hours	Glycolaldehyde traces	Glycolic acid present, oxalic acid 3.1	Oxalic acid 1.26
5	1,2-Propanediol 0.40, NO_2 0.60	20°, 24 hours	Hydroxyacetone 0.01	Pyruvic acid present	Hydroxyacetone 0.0025
6	1,2-Propanediol 0.40, NO_2 0.60, H_2O 0.17	20°, 24 hours	Hydroxyacetone 0.04	Pyruvic acid present	Hydroxyacetone 0.01
7	Methyl glucoside 0.127, NO_2 0.39	20°, 24 hours	Hydroxy keto compound 1.24	Methyl glucosiduronic acid 10.0	Glucosiduronic acid 8.0*, keto compound derived from glucosiduronic acid 0.97
8	Methyl glucoside 0.09, NO_2 0.33, H_2O 0.04	20°, 24 hours	Hydroxy keto compound 2.6	Methyl glucosiduronic acid 6.93	Glucosiduronic acid 7.0**, keto compound derived from glucosiduronic acid 10.8

* 2.34 g of barium salt was isolated.
** 1.52 g of calcium salt was isolated.

Investigation of Water-soluble Fraction. The total acidity was determined, and part of the neutralized aqueous solution was vacuum-distilled, the volatile aldehydes being trapped in sodium bisulfite solution. The residue was then acidified, and the volatile acids were trapped in 0.5 N NaOH. Aldehydes and volatile acids (formic, acetic, nitrous, and nitric) were determined in the respective distillates. The same determinations were carried out with part of the solution in which nitrite ions had been destroyed by addition of urea. The residue from the distillation contained compounds of low volatility, which were identified by the preparation of derivatives, by quantitative methods of estimation, and, in some cases, by paper chromatography. The results of the investigation of the composition of the oxidation products are given in Table 1.

Investigation of Reaction Products Soluble in Carbon Tetrachloride. After being carefully washed with water and dried over sodium sulfate, solutions of the reaction products in carbon tetrachloride were yellowish. Nitrite ions were formed when the solutions were treated with alkali. The solutions were investigated for the presence of nitric and nitrous esters before and after hydrolytic treatment with alkali at room temperature. In the analysis, 5-ml portions of the carbon tetrachloride solution were measured into two 100-ml measuring flasks, and 20 ml of water was added to each portion.

Into one of the flasks, 1 ml of 40% NaOH was added in order to hydrolyze the esters. The solutions were allowed to stand for 24 hours at room temperature and then brought to 100 ml with water. Nitric acid was determined in this solution colorimetrically with "disulfophenolic" acid [7], and nitrous acid was determined colorimetrically by the 1-naphthol reaction [8]. In some cases, the contents of keto groups and of individual ketones were also determined (Table 2).

TABLE 2
Investigation of Fractions dissolved in Carbon Tetrachloride

Experiment No.	Substance oxidized	Amount of HNO_3 (mg-equiv)		Amount of HNO_2 (mg-equiv)		Found (mg-equiv)	
		Before hydrolysis	After hydrolysis	Before hydrolysis	After hydrolysis	Before hydrolysis	After hydrolysis
						Acetone	
1	Isopropyl alcohol	16.9	1.9	Traces	Several times as great	10.1	13.2
2	Isopropyl alcohol in presence of moisture	13.3	2.8	Traces	Ditto	25	32.7
						Glycoaldehyde	
3	Ethylene glycol	10.8	12.1	Nil	0.20	Nil	Present
4	Ethylene glycol in presence of moisture	3.5	1.9	2.8	8.7	"	"
						Hydroxyacetone	
5	1,2-Propanediol	Nil	0.15	Nil	0.23	Nil	Present
6	1,2-Propanediol in presence of moisture	0.5	2.3	0.19	1.9	"	"
7	Methyl glucoside	Nil	Nil	Nil	Nil	*	—
8	Methyl glucoside in present of moisture	"	"	"	"	—	—

* In the oxidation of methyl glucoside the nitric esters were in the water-soluble fraction. Before hydrolysis the NO_2 content was nil, and after hydrolysis it was 16 mg-equiv.

Oxidation of Isopropyl Alcohol. After the oxidation of isopropyl alcohol, acetone was determined in the distillate of the aqueous layer by the salicylaldehyde colorimetric method (Fabrinf's reaction [9]). This reaction is specific for ketones containing the grouping $-CH_2-CO-CH_2-$, and acetaldehyde and alcohols do not interfere.

The yield of acetone corresponded to 4.7% of the isopropyl alcohol taken when water was absent, and to 12% when water was present. The formation of acetone was confirmed by the preparation of its 2,4-dinitrophenylhydrazone, of which 70 mg were obtained, m.p. 125.5° (the literature gives 126°).

	Found %: N 23.41 (Dumas)
$C_9H_{10}O_4N_4$	Calculated %: N 23.68

Qualitative reactions showed the presence of formic and acetic acids in the volatile-acid distillate. Quantitative determination of formic acid with mercuric chloride gave 0.3 mg-equiv (0.0006%) for oxidation in an anhydrous medium and 0.16 mg-equiv (0.0003%) for oxidation in presence of water.

In the analysis of the fraction soluble in carbon tetrachloride, it was found that it gave a positive reaction for nitrite with the Griess reagent, and the color was more intense when a preliminary treatment with alkali was given. When the solution was made alkaline and allowed to stand, it became acid again owing to the hydrolysis of nitric or nitrous esters. It was established that, after alkaline hydrolysis, the nitric acid content (free and bound as ester) fell and nitrous acid appeared, although this was usually present only in traces before hydrolysis.

Nitrous acid could be formed by hydrolysis of isopropyl nitrite with regeneration of isopropyl alcohol, and also by oxidative hydrolysis of isopropyl nitrate. In the latter case acetone would be formed. Colorimetric determinations showed that, in the experiment under anhydrous conditions, 13.2 mg-equiv of acetone was formed after hydrolysis of the fraction soluble in carbon tetrachloride, and in the experiment in presence of water 32.7 mg-equiv of acetone was formed. There was therefore an appreciable amount of isopropyl nitrate in the carbon tetrachloride solution, and on hydrolysis this was converted into acetone with formation of nitrous acid.

$$CH_3-\underset{\underset{ONO_2}{|}}{CH}-CH_3 \xrightarrow{OH^-} CH_3COCH_3 + NO_2' + H_2O.$$

Oxidation of Ethylene Glycol. The aqueous fraction from the oxidation of ethylene glycol did not give aldehyde reactions and therefore did not contain glycolaldehyde. After removal of volatile acids under reduced pressure, oxalic acid was precipitated as the calcium salt in presence of ammonia and ammonium chloride. The precipitate was washed through with dilute hydrochloric acid, and oxalic acid was determined by titration with 0.1 N $KMnO_4$.

Fig. 1. Chromatograms: A) experimental solution; B) glycolic acid

In the oxidation in an anhydrous medium, the aqueous fraction contained only traces of oxalic acid, whereas in the experiment in presence of water, 0.140 mg of oxalic acid was found (1.15% on the amount of ethylene glycol taken). Apart from oxalic acid, glycolic acid was detected by paper chromatography (solvent: a 10 : 2 : 8 mixture of butyl alcohol, formic acid, and water; developer: Bromophenol blue) (Fig. 1).

When the fraction soluble in carbon tetrachloride was hydrolyzed with 2% caustic soda in the cold, nitrous acid was formed and the solution gave a positive result with Schiff's reagent. In an acid medium no hydrolysis occurred and no nitrous acid was formed.

Oxidation of 1,2-Propanediol. The aqueous fraction from the oxidation of 1,2-propanediol gave no reaction with Schiff's reagent. The reaction with Fehling's solution was positive in the cold, as also was Benedict's reaction for the hydroxy ketone grouping. Practically no volatile acids were formed. The residue remaining after the removal of volatile compounds was heated with an alcoholic solution of 2,4-dinitrophenyl-

hydrazine and hydrogen chloride, and an osazone, m.p. 290.5-300° (after recrystallization from ethyl acetate), was isolated. For the osazone of hydroxyacetone the literature gives m.p. 300°. In Experiment 5 the amount of osazone isolated corresponded to 0.67 mg of hydroxyacetone, and in Experiment 6 it corresponded to 2.72 mg.

Hydrazones of keto acids were extracted by means of sodium carbonate solution from the mother liquor left after the crystallization of the osazone of hydroxyacetone. After acidification and extraction of the solution with ethyl acetate, a small amount of hydrazones was obtained. In order to test for the presence of the 2,4-dinitrophenylhydrazone of pyruvic acid, the material was investigated chromatographically against a synthetic preparation (m.p. 218°) obtained by the condensation of pyruvic acid with 2,4-dinitrophenylhydrazine. In the separation on paper (solvent: butyl alcohol saturated with 3% ammonia solution), two pairs of spots were obtained; these corresponded exactly with one another and with data in the literature [10], according to which this hydrazone, like free pyruvic acid, gives two spots in paper chromatography (Fig. 2).

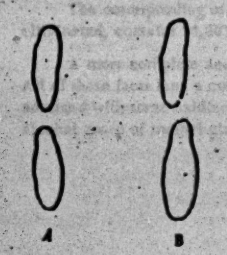


Fig. 2. Chromatograms: A) experimental solution; B) pyruvic acid

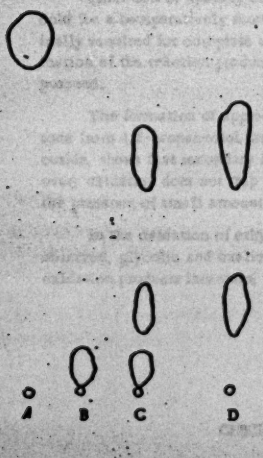


Fig. 3. Chromatograms: A) lactic acid; B) nitric acid; C) experimental solution; D) pyruvic acid

Direct chromatographic separation of the aqueous fraction of acids on paper showed the presence of pyruvic and nitric acids in the oxidation products of 1,2-propanediol; no lactic acid was detected (Fig. 3). In the fraction that dissolved in carbon tetrachloride, an appreciable amount of nitrous acid was formed after hydrolysis with 2% caustic soda in the cold. Before hydrolysis the colorimetric reaction with salicylaldehyde for hydroxyacetone was negative, but after hydrolysis it was positive, thus indicating the formation of hydroxyacetone in the hydrolysis.

Oxidation of Methyl α-Glucoside. In the oxidation, 2.5 moles of nitrogen dioxide were taken for each mole of the glucoside. As oxidation proceeded the appearance of the suspension of methyl glucoside in carbon tetrachloride changed and it gradually became a sticky greenish sirup. This was allowed to stand for 24 hours, nitrogen oxides were removed in the cold under reduced pressure, and the product was treated with water, yielding an aqueous layer, which contained the bulk of the reaction products, and a carbon tetrachloride layer, which did not contain an appreciable amount of oxidized compounds.

There were no aldehydes and voltaile organic acids in the aqueous layer. After the content of nitric and nitrous acids had been taken into account, the acidity of the aqueous layer was still high, which indicated that much of the glucoside had been oxidized. The aqueous layer gave an intense reaction with Benedict's reagent for α-hydroxy ketone groupings [11], the amount of which was found to be 1.24 mg-equiv (0.97% of the amount calculated for the oxidation of one alcohol group) for reaction in an anhydrous medium and 9.6 mg-equiv (10.8%) for reaction in presence of water. When allowed to stand in an alkaline medium, the aqueous fraction became acid, the extent of the acidification being 12% of the acidity of the original solution. As acidity developed there was an increase in the content of nitrite ions.

Methyl glucosiduronic acid was isolated in Experiment 7 as the barium salt (1.74 g from one half of the volume of the reaction products) and in Experiment 8

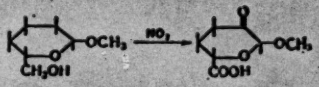
as the calcium salt (1.52 g). The salts were not purified from inorganic salts, but were used directly for the preparation of osazones in order to prove the presence of keto derivatives. According to the analysis of the barium salt, it contained hydroxy ketone groupings in an amount corresponding to 2.7% admixture of an oxidized methyl glucosiduronic acid containing a keto group to the main mass of methyl glucosiduronic acid.

When the barium and calcium salts were treated with a solution of 2,4-dinitrophenylhydrazine in aqueous 2 N HCl at 5-7°, osazones of high melting point (above 340°) were obtained; they gave a bluish-violet color with alkalis, and they were soluble in ethyl acetate.

Found %: N 19.74 (osazone from Ba salt)
Found %: N 19.57; 19.93 (osazone from Ca salt)
$C_{25}H_{28}O_{13}N_8$. Calculated %: N 19.86

The corresponding osazone of glucuronic acid, which could be formed if the glucoside methyl were to be eliminated, contains 20.30% N, i.e. appreciably more than the amount found.

A more complete analysis of the osazones obtained could not be carried out owing to their small amount. All of these facts lend a considerable measure of probability to the suggestion that the glucosiduronic acid was admixed with some oxidized glucosiduronic acid containing a keto group formed by the oxidation of a secondary alcohol group of methyl glucoside.

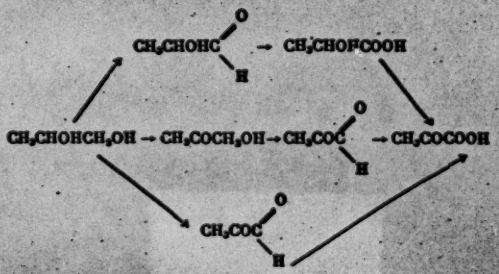


Discussion of Experimental Results

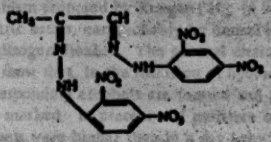
Oxidation of hydroxy compounds with nitrogen dioxide under the given experimental conditions - in the cold for a comparatively short time (24 hours) with half of the amount of nitrogen dioxide that would be theoretically required for complete oxidation - does not result in far-reaching decomposition. On this account, examination of the reaction products enables us to determine the primary direction in which the oxidation processes proceed.

The formation of appreciable amounts of acetone (up to 12%) from isopropyl alcohol and of hydroxyacetone from 1,2-propanediol, and also the formation of hydroxy ketone groupings in the oxidation of methyl glucoside, shows that secondary alcohol groups are oxidized by nitrogen dioxide under the given conditions. Moreover, oxidation does not stop at this stage, but continues further with scission of a C–C bond, as indicated by the presence of small amounts of formic and acetic acids in the reaction products.

In the oxidation of ethylene glycol the successive stages in the oxidation of the two alcohol groups can be observed, glycolic and oxalic acids being formed. In the oxidation of 1,2-propanediol, the number of possible oxidation products increases:

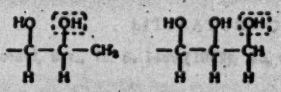


From the reaction products an osazone was isolated which corresponds in analysis to:



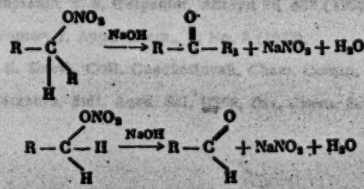
This osazone could be formed from any of the three carbonyl compounds given in the scheme. However, as the solution does not give a reaction for aldehyde groups while giving a strongly marked reaction for hydroxy ketone groupings, the question is resolved in favor of hydroxyacetone as one of the primary products of the oxidation of 1,2-propanediol with nitrogen dioxide. Direct colorimetric determination of hydroxyacetone in the reaction products gave a content corresponding to 0.002-0.01% of the theoretically possible content for the oxidation of one hydroxy group per molecule. Since 1,2-propanediol has a glycol grouping in which one hydroxyl is primary and the other secondary, it was of interest to determine which of the two alcohol groups is preferentially oxidized. One might expect that lactic acid would be the main reaction product, and pyruvic acid would be a secondary product. However, the presence among the reaction products of hydroxyacetone and pyruvic acid and the absence of detectable amounts of lactic acid indicate that the oxidation processes proceed in a different way, the predominating process being the oxidation of the secondary alcohol group. A different picture is to be observed in the oxidation of methyl glucoside: here, the main direction of reaction in an anhydrous medium is the oxidation of the primary alcohol group at the terminal carbon atom (to the extent of 8%). The oxidation of secondary alcohol groups occurs only to a slight extent (not more than 1%), as our experiments have shown, and only in the presence of water - when far-reaching decomposition sets in - are hydroxy ketone groupings formed to an appreciably greater extent (10-11%).

The effect of molecular structure is to be seen in this difference in order of oxidation: when there is a methyl group in proximity to a hydroxyl, the secondary alcohol group is more readily oxidized, but in carbohydrates, in which all carbons carry OH groups, the primary alcohol group is oxidized first:



Hence, 1,2-propanediol gives hydroxyacetone as main product, whereas methyl glucoside gives methyl glucosiduronic acid.

As we have shown, in the fraction of the oxidation products that passes into carbon tetrachloride (or into water, in the case of methyl glucoside), there are compounds that eliminate nitrous acid when treated with alkali in the cold. These could be nitrous or nitric esters of oxidizable alcohols. As it is found that hydrolysis is accompanied by the formation of ketones or aldehydes (acetone from isopropyl alcohol, hydroxyacetone from 1,2-propanediol, and an aldehyde from ethylene glycol), it is probable that oxidative hydrolysis of nitric esters occurs, in accordance with the scheme:



Hence, the mechanism proposed by Kenyon [12], in which the oxidation of cellulose proceeds with intermediate formation of nitric esters, can probably be extended to the oxidation of hydroxy compounds of low molecular weight with nitrogen dioxide. The general character of this reaction follows also from Titov's investigations [13], which show that, in the nitration of hydrocarbons, in addition to nitro derivatives nitric and nitrous esters of the corresponding alcohols are formed and are subsequently oxidized. In our experiments, the effect of water was very marked; in presence of moisture oxidation always proceeded more vigorously and the yields of oxidation products were higher than in a dry anhydrous solvent. This fact can also be interpreted in the light of the proposed oxidation mechanism, in accordance with which the primary stage of the reaction is the formation of a nitric ester by the action of nitric acid formed from nitrogen dioxide and traces of moisture.

SUMMARY

1. The main product in the oxidation of isopropyl alcohol by nitrogen dioxide at room temperature is acetone. In different experiments the yield of acetone varies from 2% to 12% on the amount of alcohol taken.

2. The oxidation of ethylene glycol with nitrogen dioxide proceeds in such a way that it is difficult to characterize the intermediate products in the oxidation. The process rapidly reaches the stage of oxalic acid formation. Oxalic and glycollic acids were identified.

3. Among the oxidation products of 1,2-propanediol, hydroxyacetone and pyruvic acid were identified. No lactic acid was found. This indicates that the predominating process is the oxidation of secondary alcohol groups.

4. A study of the oxidation of methyl α-glucoside with nitrogen dioxide under the same conditions showed that not only primary, but also secondary alcohol groups are oxidized. In the methyl glucosiduronic acid obtained from the products as the barium and calcium salts, another compound, containing a hydroxy ketone grouping, was present as impurity. An osazone was prepared from this compound, and it corresponded in analysis to the osazone of an oxidized methyl glucosiduronic acid containing a keto group.

5. It was established that the process of oxidizing alcohols of low molecular weight and methyl glucoside with nitrogen dioxide proceeds through the stage of a nitric ester, which undergoes oxidative hydrolysis with elimination of nitrous acid.

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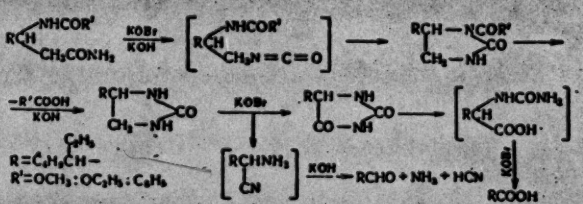
NEW DATA ON THE HOFMANN REACTION

COMMUNICATION 4. ACTION OF HYPOBROMITE ON DIASTEREOISOMERIC 3-(ACYLAMINO)-4-ETHYLOCTANAMIDES

V. M. Rodionov*, V. K. Zvorykina, and N. E. Kozhevnikova

In previous investigations on the Hofmann reaction of amides of β-acylamino acids, namely derivatives of 3-aminononanoic [1], β-aminohydrocinnamic [2], and β-amino-3,4-methylenedioxyhydrocinnamic [3] acids, it was shown that acids containing aromatic and aliphatic radicals behave differently. Although in the first stage of the reaction the same type of product is formed in both cases by intramolecular rearrangement of the isocyanate - the corresponding 1-acyl-5-alkyl(or aryl)-2-imidazolidinone - the second stage - hydrolysis of the acyl group and formation of a 5-alkyl (or aryl)-2-imidazolidinone - proceeds considerably more rapidly in the case of an amino acid containing an aromatic radical. The further transformation of the imidazolidinone, leading finally to a carboxylic acid, proceeds, in the case of a β-amino acid containing an aliphatic radical, through the stages of the formation of an alkylhydantoin, an α-ureido acid, and an α-amino acid, but in the case of a β-amino acid containing an aromatic radical through the intermediate formation of an aroylurea and a 5-aryl-Δ^4-1,3,4-oxadiazolin-2-one.



With the object of confirming previous observations, we carried out Hofmann's reaction with amides of benzoyl and alkoxycarbonyl derivatives of two diastereoisomeric 3-amino-4-ethyloctanoic acids which we have synthesized and denoted by the symbols A_1 and A_2 [4]. Reaction with the benzoyl derivative stopped at the stage of the imidazolidinone. As by-products, both isomers gave high-melting neutral substances corresponding in analysis to alkylarylureas. Reaction of the isocyanate in this direction is generally observed when the amides are sparingly soluble, and we have observed it also in a previous investigation [5]. When the Hofmann reaction was carried out with amides of alkoxycarbonyl derivatives of the isomers A_1 and A_2, products obtained were the 1-alkoxycarbonyl-5-(1-ethylpentyl)-2-imidazolidinone, 4-(1-ethylpentyl)-2-imidazolidinone, 5-(1-ethylpentyl)-hydantoin, and 2-ethylhexanoic acid. Also, when the oil remaining after the separation of these compounds was hydrolyzed, the presence of 2-ethylhexanal, ammonia, and hydrogen cyanide was detected in the product. From

* Deceased.

this it may be inferred that, as in the case of other aliphatic β-amino acids, for the new representatives of this class of compound that we have studied, the process proceeds in accordance with the general scheme that we proposed in a previous paper [1].

EXPERIMENTAL

Hofmann Reaction with 3-Benzamido-4-ethyloctanamide (A_2 Isomer)

The amide (4 g) was gradually added to a hypobromite solution prepared from 1.75 g of bromine, 6.45 g of caustic potash, and 45 ml of water at −7 to −10°*. When solution was complete, stirring was continued for one hour. The solution was then heated to 65° and cooled rapidly. The solution and the precipitate that had formed were treated with ether.

Isolation of Benzoic Acid. Acidification of the alkaline solution yielded 0.35 g of benzoic acid, m.p. 122°.

Isolation of Substance of M.p. 219°. The ether-insoluble precipitate was boiled with water and crystallized from alcohol. The product, amounting to 0.4 g, melted at 219° (fine colorless prisms).

		Found %	C	71.02; 70.93;	H	8.74; 8.67;	N	9.30; 9.45
$C_{24}H_{30}O_4N_4$.	Calculated %	C	70.59;	H	8.65;	N	9.67	

Isolation of 1-Benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_2. The ether solution was extracted several times with 12% hydrochloric acid, washed, first with water, then with caustic soda solution, and again with water, and dried with sodium sulfate. After part of the ether had been distilled off, 1.2 g of a substance of m.p. 153°, was obtained.

		Found %	C	70.98; 70.79;	H	8.59; 8.36;	N	9.70; 9.69
$C_{18}H_{26}O_2N_2$.	Calculated %	C	70.83;	H	48.33;	N	9.72	

Further removal of ether enabled about 0.5 g more of the imidazolidinone A_2 to be isolated. When ether was removed completely there remained an oil, and treatment of this with a mixture of diethyl ether and petroleum ether gave 0.04 g of a substance melting at 143° which did not appear to be the imidazolidinone A_2 isolated as indicated above.

Found %	N	11.48;	11.51	

This substance was not studied in detail.

Isolation of 4-(1-Ethylpentyl)-2-imidazolidinone A_2. Cooling of the hydrochloric acid solution and careful addition of solid caustic potash yielded 0.29 g of a substance of m.p. 140-141° (needles from a mixture of diethyl ether and petroleum ether).

		Found %	C	65.31;	H	10.50;	N	15.47; 15.39
$C_9H_{18}ON_2$.	Calculated %	C	65.21;	H	10.86;	N	15.21	

Hydrolysis of 1-Benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_2. Heating of 0.3 g of the benzoylimidazolidinone A_2 with 20% caustic soda for four hours in a water bath yielded 0.06 g of benzoic acid, m.p. 121°, 0.07 g of the above described 4-(1-ethylpentyl)-2-imidazolidinone, m.p. 139-140°, and 0.01 g of the above-described substance of m.p. 148°.

Hofmann Reaction with 3-Benzamido-4-ethyloctanamide (A_1 Isomer)

When the reaction was carried out with 6.81 g of amide under the conditions described for the A_2 isomer, acidification of the alkaline solution yielded 0.21 g of benzoic acid. The ether-insoluble precipitate gave 0.43 g of a substance of m.p. 204°.

* Experimental investigation of the Hofmann reaction applied to 3-benzamido-4-ethyloctanamide A_1 was carried out by N. E. Kozhevnikova. All of the remaining experimental work was carried out by V. K. Zvorykina.

Found %: C 71.83; 72.01; H 8.85; 9.00; N 9.78; 9.69

The ether solution yielded 2.55 g of 1-benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_2, m.p. 141-142° (needles from ether). A mixture with the A_2 isomer melted at 114-116°.

Found %: C 70.64; 70.52; H 8.38; 8.52; N 9.85; 9.92

The hydrochloric acid solution yielded 0.25 g of 4-(1-ethylpentyl)-2-imidazolidinone A_2, m.p. 141-142° (colorless needles from ether). A mixture with the A_1 imidazolidinone melted at 117-123°.

Found %: C 65.15; 65.29; H 10.92; 10.99; N 15.51; 15.34

Hydrolysis of 1-benzoyl-5-(1-ethylpentyl)-2-imidazolidinone A_1 gave benzoic acid and 4-(1-ethylpentyl)-2-imidazolidinone A_2, m.p. 139-140°.

Hofmann Reaction with 4-Ethyl-3-(methoxycarbonylamino)octanamide (A_1 Isomer)

The amide (20 g) was added in small portions with stirring to a cooled (−3°) solution of hypobromite prepared from 40 g of caustic potash, 280 ml of water, and 10.3 ml of bromine. When solution was complete (about three hours), stirring was continued for one hour at room temperature and the flask was then transferred to a water bath and the temperature raised to 65° (at 55° a spontaneous rise in temperature occurred). The flask was then rapidly immersed in a cooling mixture. The alkaline solution containing precipitated oil was extracted with ether, and the ether extract was extracted several times with 12% hydrochloric acid.

Isolation of 5-(1-Ethylpentyl)hydantoin A_1 and 2-Ethylhexanoic Acid. When the alkaline solution was acidified an oil separated and was extracted with ether; the ether solution was washed with water and dried with sodium sulfate. After removal of ether there remained 1.3 g of oil, which partially crystallized; when this was treated with 10 ml of heptane, crystals were precipitated, which were twice reprecipitated from an alkaline solution with acid and then recrystallized from water. The yield of the hydantoin A_1 was 0.09 g, m.p. 140-141°.

Found %: C 60.66; 60.22; H 9.20; 9.03; N 14.36; 14.25

$C_{10}H_{18}O_2N_2$. Calculated %: C 60.60; H 9.09; N 14.14

When the heptane was distilled off, 0.8 g of liquid 2-ethylhexanoic acid remained; it was characterized as its amide, m.p. 104-105°.

Isolation of 4-(1-Ethylpentyl)-2-imidazolidinone A_1. The hydrochloric acid solution was rendered alkaline with solid potassium hydroxide, cooling being applied. The imidazolidinone obtained (0.75 g) melted at 141-142° (needles from ether) and was identical with that described above.

Isolation of 5-(1-Ethylpentyl)-1-methoxycarbonyl-2-imidazolidinone A_1. After removal of ether, 9 g of oil was obtained, and this crystallized when seeded with 4-(1-ethylpentyl)-2-imidazolidinone. When a little ether was added, 1.2 g of the imidazolidinone A_1 was precipitated. Addition of heptane to the filtrate resulted in the precipitation of a further 0.2 g of the same substance, and after several hours the clear filtrate gave a precipitate of 1.19 g of 5-(1-ethylpentyl)-1-methoxycarbonyl-2-imidazolidinone A_2, m.p. 84.5-85° (from a mixture of diethyl ether and petroleum ether). After the hydrolysis of this compound by boiling it with 20% caustic soda, 4-(1-ethylpentyl)-2-imidazolidinone A_1 was isolated.

Found %: C 59.63; 59.47; H 9.37; 9.45; N 11.79; 11.69

$C_{12}H_{22}O_3N_2$. Calculated %: C 59.50; H 9.09; N 11.57

The oil remaining after the separation of the imidazolidinones was hydrolyzed by heating it with 7.5% caustic soda solution. It was shown that hydrogen cyanide, ammonia, and 2-ethylhexanal (identified as the dinitrophenylhydrazone) were formed.

Hofmann Reaction with 3-(Ethoxycarbonylamino)-4-ethyloctanamide (A_2 Isomer)

The reaction was carried out with 11 g of the amide. The experimental conditions and the methods of isolating the products were similar to those described for the analogous A_1 compound.

Isolation of 5-(1-Ethylpentyl)hydantoin A_2 and 2-Ethylhexanoic Acid. When the alkaline solution was acidified, an oil was precipitated, and when petroleum ether was added to this, 0.078 g of the hydantoin A_2, m.p. 172°, was obtained (purification as for the A_1 isomer).

	Found %:	C 60.49;	60.30;	H 9.37;	9.13;	N 13.90;	14.11
$C_{12}H_{22}O_2N_2$.	Calculated %:	C 60.60;		H 9.09;		N 14.14	

After removal of petroleum ether there remained an oil. Steam distillation of this yielded 0.17 g of 2-ethylhexanoic acid, which was identified as the amide.

Isolation of 4-(1-Ethylpentyl)-2-imidazolidinone A_2. The hydrochloric acid extract yielded 1.33 g of the imidazolidinone A_2, m.p. 140-141°, already described above.

Isolation of 1-Ethoxycarbonyl-5-(1-ethylpentyl)-2-imidazolidinone A_1. After partial removal of ether the solution gave 1.15 g of 1-ethoxycarbonyl-5-(1-ethylpentyl)-2-imidazolidinone A_1, m.p. 88° (colorless plates from ether). Its alkaline hydrolysis gave 4-)1-ethylpentyl)-2-imidazolidinone A_2, m.p. 140°.

After complete removal of ether, 6 g of a noncrystallizing oil was obtained. One half of this was hydrolyzed with 7% caustic soda solution, and the formation of hydrogen cyanide, ammonia, and 2-ethylhexanal was established. In addition, 2.3 g of 4-(1-ethylpentyl)-2-imidazolidinone A_2, m.p. 139-140°, was isolated.

SUMMARY

1. A study was made of the action of hypobromite on the diastereoisomers A_1 and A_2 of 3-benzamido- and 3-(alkoxycarbonylamino)-4-ethyloctanamides.

2. From the products obtained from the benzamido compounds, the stereoisomeric 4-(1-ethypentyl)--2-imidazolidinones and 1-benzoyl-5-(1-ethylpentyl)-2-imidazolidinones, and also benzoic acid, were isolated.

3. From the products obtained from the alkoxycarbonylamino compounds, the stereoisomeric 1-alkoxycarbonyl-5-(1-ethylpentyl)-2-imidazolidinones, 4-(1-ethylpentyl)-2-imidazolidinones, and 5-(1-ethylpentyl)-hydantoins, and also 2-ethylhexanoic acid, were isolated. When the oil remaining after the separation of the above compounds was hydrolyzed, hydrogen cyanide, ammonia, and 2-ethylhexanal were present among the products.

4. The results obtained confirm the correctness of the scheme that we have proposed previously for the Hofmann reaction with amides of acylated β-amino acids.

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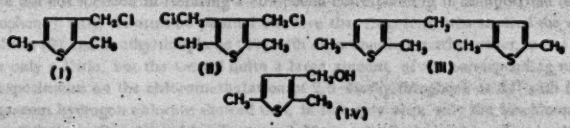
CHLOROMETHYLATION OF 2,5-DIMETHYLTHIOPHENE

Ya. L. Goldfarb and M. S. Kondakova

Chloromethylation is one of those reactions that are readily affected by various factors. Change of temperature or condensing agent, replacement of formaldehyde by paraformaldehyde, etc., may not only reduce or increase the yield of the product, but may also alter its identity. Lock, in his detailed investigation of the chloromethylation of benzene [1], showed, in particular, the dependence of the yield of benzyl chloride on the zinc chloride content of the reaction mixture and on the duration of the process; the yield of benzyl chloride attains a maximum value (70%) in a certain interval of time and then falls almost to zero as the duration of the experiment increases, this being accompanied by a rapid increase in the yield of diphenylmethane. The peculiar "sensitivity" of this reaction may be the cause of discrepancies in results on chloromethylation obtained by different investigators. As an example we may point out that Lock could not confirm Tschunkur and Eichler's results on the synthesis of benzyl chloride by the chloromethylation method. We came across a similar situation in the chloromethylation of 2,5-dimethylthiophene by the action of formaldehyde and hydrogen chloride in hydrochloric acid under cooling in accordance with the procedure of Buu-Hoi and Nghyen Hoan [2]. According to these investigators, under these conditions a little 3-(chloromethyl)-2,5-dimethylthiophene is formed, but the main product is 3,3'-methylenebis[2,5-dimethylthiophene] (III), m.p. 72°. In our experiments we obtained approximately equal amounts of the mono(chloromethyl) derivative (I) and 3,4-bischloromethyl-2,5-dimethylthiophene (II), but did not succeed in isolating any of the substituted methylenedithiophene (III) of m.p. 72°.

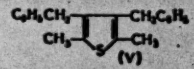


The same two compounds (I) and (II), but in somewhat different proportions, were formed in the chloromethylation of 2,5-dimethylthiophene with chloromethyl methyl ether in glacial acetic acid. In order to confirm the structure of the compound that we regarded as 3-(chloromethyl)-2,5-dimethylthiophene, it was converted via the acetoxymethyl compound into the corresponding alcohol, which, according to its composition and the properties of the urethan derived from it, was identical with 2,5-dimethyl-3-thiophenemethanol (IV), which was prepared by Brown and Blanchette [3] by the reduction of 2,5-dimethyl-3-thiophenecarboxaldehyde. The compound (II), the product of the bischloromethylation of 2,5-dimethylthiophene, was obtained in a yield of about 65% by the chloromethylation of 2,5-dimethylthiophene with paraformaldehyde and hydrogen chloride at 50°, i.e. under conditions almost identical with those described by Gaertner and Tonkyn [4]. It must be pointed out that, in this case also, we failed to detect a product of composition corresponding to the methylenedithiophene of structure (III). We isolated a very small amount of a chlorine-containing product melting at 173° which was identical in properties with the substance obtained by the chloromethylation of a compound that we have isolated in the course of this work (see below); this latter compound melts at 48.5° and corresponds in composition to the compound (III) mentioned above.

We repeatedly prepared the bischloromethyldimethylthiophene (II) by the method indicated, and in all of the experiments it melted, after recrystallization, at 67-68.5°; sublimation did not affect its melting point.

On the other hand, in the paper cited by Gaertner and Tonkyn, a melting point of 73.4° is given for 3,4-bischloromethyl-2,5-dimethylthiophene. This discrepancy might be caused by the constant presence of an impurity, which could arise from the fact that we did not prepare the original dimethylthiophene from 2,5-hexanedione, but by King and Nord's method [5], i.e. the formulation of 2-methylthiophene and subsequent reduction. In its turn, 2-methylthiophene was prepared by the same method from thiophene. It was impossible to be certain that this method gave a pure compound and not a mixture of 2,5- and 2,3-dimethylthiophenes. In order to resolve this doubt we prepared a ketone by the action of acetyl chloride on the synthesized dimethylthiophene and a dinitro derivative by the method of Steinkopf and coworkers [6]. The melting points of the latter and of the oxime of the former corresponded with data in the literature for 2,5-dimethyl-3,4-dinitrothiophene and the oxime of 2,5-dimethyl-3-thienyl methyl ketone, respectively. It was established in this way that the dimethylthiophene that we used was mainly, if not entirely, 2,5-dimethylthiophene.

In order to make sure that the bischloromethyldimethylthiophene of m.p. 68° that we obtained was indeed a tetrasubstituted thiophene having the properties of a bifunctional compound, we investigated some of its reactions. The compound was reduced with stannous chloride [7]; the resulting substance of composition $C_8H_{10}S$ was not acetylated when treated with acetyl chloride in presence of stannic chloride and was identical in physical properties with the tetramethylthiophene described by Gaertner and Tonkyn [4]. When the substance of m.p. 68° was treated with benzene in presence of aluminum chloride, a compound was formed which corresponded in composition with 3,4-dibenzyl-2,5-dimethylthiophene (V)



(V)

which we obtained also by the condensation of 2,5-dimethylthiophene with benzyl alcohol in presence of sulfuric acid [8]. These facts are in accord with the view that the substance of m.p. 68° is indeed a bifunctional derivative.

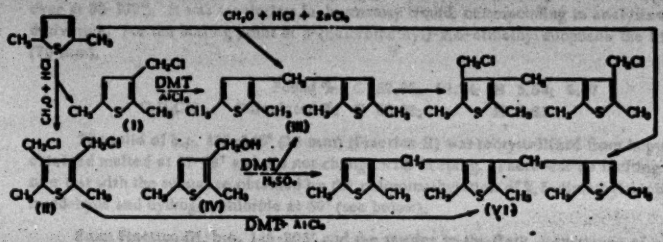
It was stated above that in chloromethylation experiments on 2,5-dimethylthiophene in the cold and at 50° we did not succeed in isolating a compound corresponding in composition to 3,3'-methylenebis[2,5-dimethylthiophene] (III). It must be pointed out here that Cagniant, who studied the chloromethylation of 2,5-diethylthiophene [9] and 2-ethylthiophene [10] with chloromethyl methyl ether, states that the first of these compounds forms only a little, but the second quite a large amount, of the corresponding substituted methylenedithiophene. Our experiments on the chloromethylation of 2,5-diethylthiophene at 30° with formaldehyde, hydrochloric acid, and gaseous hydrogen chloride showed that, in this case also, only the bischloromethyl derivative is formed, this, however, being accompanied by the mono(chloromethyl) derivative when cooling is applied. Finally, it must be pointed out also that in the chloromethylation of 2,5-di-tert-butylthiophene in acetic acid*, formation of the corresponding derivative of 3,3'-methylenedithiophene was again not observed, only the bischloromethyl derivative being isolated.

A different picture is observed when 2,5-dimethylthiophene is chloromethylated in presence of zinc chloride. In this case two crystalline substances are formed, one corresponding in composition to (III) and the other to 3,4-bis(2,5-dimethyl-3-thenyl)-2,5-dimethylthiophene (VI):

(VI)

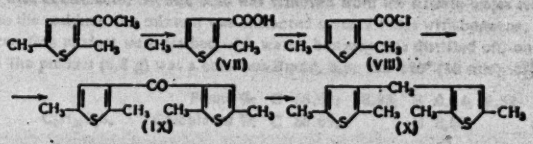
* The chloromethylation of 2,5-di-tert-butylthiophene was studied in our Laboratory by M. L. Kimmalova.

However, the first of these compounds differed in melting point (48.5°) from the compound described by Buu-Hoi and Nghyen Hoan as 3,3'-methylenebis[2,5-dimethylthiophene], for which they obtained a melting point of 72°. This fact prompted us to seek other ways of preparing the compound (III), and the compound (VI) that accompanied it, with the object of making a comparison of properties. The scheme given below illustrates the results obtained:



in which DMT denotes 2,5-dimethylthiophene. From this scheme and the results given in the experimental part it will be seen that all of the methods selected for the preparation of the substituted methylenedithiophenes (III) and (VI) give identical compounds. Since the structure of one of the starting materials, 2,5-dimethyl-3-thiophenemethanol was established by an independent method (see above), the structure (III) for the product of m.p. 48.5° may be considered to be established.

As, however, the causes of the nonidentity of the melting points of our preparation and previously described preparations of 3,3'-methylenebis[2,5-dimethylthiophene] still remained obscure, we decided to prepare it by yet another method, in accordance with the scheme:



The first three stages of this process have been described by Buu-Hoi and Nghyen Hoan [11], and only the reduction of the ketone (IX) was carried out by us for the first time. We again obtained the compound of m.p. 48.5°, but at the same time we found some new discrepancies between constants observed by us and those given in the paper cited, namely those for the acid chloride (VIII) and the ketone (IX). The causes of these and previously mentioned discrepancies are at present obscure.

EXPERIMENTAL

1. Chloromethylation of 2,5-Dimethylthiophene with the aid of Formaldehyde and Hydrogen Chloride. A mixture of 10 g of 2,5-dimethylthiophene, 50 ml of concentrated hydrochloric acid, and 14 ml of 37% formaldehyde was prepared in a flask cooled in an ice bath, and a powerful current of hydrogen chloride was passed in for one hour. The temperature of the mixture gradually rose to 16°. At the end of one hour the reaction mixture was poured into ice water and extracted several times with benzene. The benzene extract was washed with water and dried over magnesium sulfate. Benzene was distilled off, and the residue was vacuum-distilled (13 mm), the following fractions being collected:

Fraction I, b.p. 98-135°; 6.7 g; colorless liquid, darkening in color when kept
Fraction II, b.p. 135-145°; 5.4 g; solid
Fraction III, b.p. 145-205°; 0.4 g; solid
Residue in flask 1.5 g

Refractionation of Fraction I gave 5.13 g of a substance boiling at 96-115° (13 mm) (the bulk of it came over at 98-102°). It was a colorless lachrymatory liquid, corresponding in analysis to the mono(chloromethyl) derivative. For the boiling point of 3-(chloromethyl)-2,5-dimethylthiophene the literature [3] gives 105-107° (20 mm).

	Found %:	C	52.65;	52.74;	H	5.54;	5.47
C_7H_9ClS.	Calculated %:	C	52.33;		H	5.61	

The solid of b.p. 135-145° (13 mm) (Fraction II) was recrystallized from heptane. The colorless crystals obtained melted at 67-68° and did not change with keeping. There was no melting-point depression in a mixture test with the substance obtained by the chloromethylation of 2,5-dimethylthiophene by means of paraformaldehyde and hydrogen chloride at 50° (see below).

From Fraction III, b.p. 145-205° and the residue in the flask, a substance of m.p. 144-157° was obtained by crystallization from heptane. The same product, although with a sharper melting point, was isolated in another experiment carried out under the same conditions apart from the amount of formaldehyde taken, which was doubled. After being recrystallized from acetone and heptane, the substance melted at 172-173°, and there was no melting-point depression in a mixture test with the product obtained by the chloromethylation of 3,3'-methylenebis[2,5-dimethylthiophene], m.p. 48.5°.

	Found %:	C	54.30;	54.14;	H	5.44;	5.46
$C_{13}H_{18}Cl_2S_2$.	Calculated %:	C	54.05;		H	5.40	

2, 2,5-Dimethyl-3-thiophenemethanol Acetic Ester. A mixture of 5.4 g of 3-(chloromethyl)-2,5-dimethylthiophene, 3 g of anhydrous sodium acetate, and 25 ml of glacial acetic acid was heated in a water bath at 60° for four hours. On the next day the precipitate of inorganic salt was filtered off and washed with acetic acid. Acetic acid was removed from the filtrate under reduced pressure, and water was added to the residue; the mixture was extracted several times with benzene. The combined benzene extracts of the reaction product were washed with water, benzene was distilled off, and the residue was vacuum-distilled. The product (3.8 g) was a colorless liquid, b.p. 125-128° (16 mm), n_D^{18} 1.5120.

	Found %:	C	58.62;	58.93;	H	6.44; 6.52;	S 17.15; 17.13
$C_9H_{12}O_2S$.	Calculated %:	C	58.69;		H	6.52;	S 17.40

3. 2,5-Dimethyl-3-thiophenemethanol. 2,5-Dimethyl-3-thiophenemethanol acetic ester (3.7 g) was added to a solution of 0.02 g of sodium in 30 ml of absolute alcohol. The mixture was kept at room temperature for 48 hours, and the alcohol was then distilled off under reduced pressure. The residue was dissolved in 30 ml of absolute alcohol and the solution was evaporated under reduced pressure to small bulk; carbon dioxide was then passed through the solution until it was saturated. The precipitate was filtered off and alcohol was distilled from the filtrate. Water was added to the residue, and the mixture was extracted with benzene. Benzene was distilled off, and vacuum distillation of the residue gave 2.1 g of a colorless liquid, b.p. 112-113° (10 mm) and n_D^{20} 1.5436, which became dark-colored on standing.

	Found %:	C	59.24;	59.44;	H	6.87; 6.88;	S 22.12
$C_7H_{10}OS$.	Calculated %:	C	58.15;		H	7.04;	S 22.53

Urethan. A mixture of 0.7 g of the alcohol and 0.6 g of phenyl isocyanate was heated in a water bath for 45 minutes. When cool, the reaction product solidified; it was recrystallized, first from hexane and then from gasoline (b.p. 60-90°). After being dried in a vacuum the urethan melted at 76-76.5°, and there was no depression in melting point in a mixture test with the urethan obtained from the alcohol prepared by the reduction of 2,5-dimethyl-3-thiophenecarboxaldehyde. For the melting point of the urethan derived from 2,5-dimethyl-3-thiophenemethanol the literature [3] gives 77-78°.

	Found %:	C	64.03;	64.29;	H	6.10; 5.97;	S	12.23; 12.22;	N 5.39
$C_{14}H_{15}NO_2S$.	Calculated %:	C	64.37;		H	5.75;	S	12.26;	N 5.35

4. Chloromethylation of 2,5-Dimethylthiophene with the aid of Paraformaldehyde and Hydrogen Chloride. A current of hydrogen chloride was passed through a mixture of 75 g of paraformaldehyde and 150 ml of concentrated hydrochloric acid at 50° until saturation was reached. Then - at the same temperature and with continued passage of a powerful current of hydrogen chloride - 27.5 g of 2,5-dimethylthiophene was added gradually to the mixture; when addition was complete the same reaction conditions were maintained for 90 minutes. When cool, the mixture was diluted with ice water. The reaction product was extracted several times with benzene. The benzene extract was washed with water, with 5% caustic potash solution, and again with water; it was then dried over calcium chloride. Benzene was distilled off, and the residue was vacuum-distilled. The bulk of the reaction product (41.2 g) came over at 130-142° (13 mm).

Recrystallization from heptane gave 34.3 g of a colorless substance, m.p. 67-68.5°. Recrystallization from heptane and hexane, and also sublimation in a current of nitrogen, did not affect its melting point.

	Found %:	C	46.20;	46.28;	H	5.02;	4.63;	Cl 33.35; 33.87
$C_9H_{10}Cl_2S$.	Calculated %:	C	45.93;		H	4.78;		Cl 33.97
	Found:	M	202					
	Calculated:	M	209					

3,4-Bischloromethyl-2,5-dimethylthiophene forms colorless crystals that remain unchanged in storage. It is soluble in benzene, ether, and acetone; less soluble in alcohol; sparingly soluble in cold heptane; and insoluble in water. It gives a precipitate of silver chloride with silver nitrate. 2,5-Dimethyl-3,4-thiophenedimethanol - which is obtained by the hydrolysis of its diacetic ester, which is itself prepared by the action of sodium acetate on 3,4-bischloromethyl-2,5-dimethylthiophene - is readily converted into 3,4-bischloromethyl-2,5-dimethylthiophene by shaking it with concentrated hydrochloric acid.

2,5-Dimethyl-3,4-thiophenedimethanol (0.8 g) was shaken with 8 ml of hydrochloric acid for 20 minutes. The mixture was then extracted with benzene. The benzene solution was washed, first with water, then with sodium bicarbonate solution, and then with water again. It was dried over magnesium sulfate. The benzene was distilled off, and 0.8 g of residue remained. Recrystallization from heptane gave 0.5 g, m.p. 67-68°, undepressed by admixture of 3,4-bischloromethyl-2,5-dimethylthiophene. Recrystallization of the 0.5 g from hexane gave 0.35 g, m.p. 67-68.5°.

5. Chloromethylation of 2,5-Dimethylthiophene with the aid of Chloromethyl Methyl Ether. A stirred mixture of 10 g of 2,5-dimethylthiophene, 14.4 g of chloromethyl methyl ether, and 30 ml of glacial acetic acid was maintained first at 0-10° for 30 minutes, and then at 23° for two hours. The reaction mixture was poured into iced water. The reaction product was extracted with benzene, and the extract was washed, first with water, then with saturated sodium bicarbonate solution, and then again with water. The solution was dried over magnesium sulfate, benzene was driven off, and the residue was vacuum-distilled, the following fractions being collected at 13 mm:

Fraction I, b.p. 96-98°; 7.6 g; colorless lachrymatory liquid
Fraction II, b.p. 110-150°; 2.5 g; which partially solidified
Fraction III, b.p. 155-184°; 1.2 g; a mixture of solid and oil
Residue in flask 1.7 g

Refractionation of Fractions I and II gave 7.3 g of a substance of b.p. 96-100° (13 mm) and a small amount of a substance of m.p. 66.5-67.5° (after recrystallization from heptane). We did not succeed in isolating a pure product from Fraction III. The product of b.p. 96-100° (13 mm) was a colorless lachrymatory liquid that darkened when kept. It had n_D^{20} 1.5482, and it was obtained in 51% yield.

6. Reaction between 3,4-Bischloromethyl-2,5-dimethylthiophene and 2,5-Dimethylthiophene in presence of Aluminum Chloride. A stirred mixture of 4.2 g of 3,4-bischloromethyl-2,5-dimethylthiophene, 5 g of 2,5-dimethylthiophene, 35 ml of carbon disulfide, and 0.2 g of aluminum chloride was maintained at room temperature for four hours and was then set aside overnight. On the next day carbon disulfide was distilled off, and water and benzene were added to the residue. The benzene layer was separated and washed, first with water, then with 5% sodium carbonate solution, and finally with water again. It was dried over magnesium sulfate. Benzene was distilled off, and 6.4 g of a solid residue was obtained which melted at 160-170° after recrystallization from heptane. When vacuum-distilled

(3-4 mm), the substance began to boil at about 200° and rapidly solidified in the side tube of the distilling flask. The product was dissolved in hot heptane, and on cooling the solution deposited colorless crystals, m.p. 174-175° (change began at 171°). A mixture test of these crystals with the substance of m.p. 174-175° obtained by the Friedel-Crafts condensation of 2,5-dimethylthiophene with 3-(chloromethyl)-2,5-dimethylthiophene showed no depression in melting point.

7. Condensation of 2,5-Dimethyl-3-thiophenemethanol with 2,5-Dimethylthiophene. A mixture of 2 g of 2,5-dimethylthiophene and 1.65 g of 2,5-dimethyl-3-thiophenemethanol was cooled with snow while addition was made of a mixture of equal weights of glacial acetic and concentrated sulfuric acids. The mixture was kept for two days at room temperature, and the reaction product, which had separated in the form of fine crystals, was filtered off. It was dissolved in hot heptane, and when the solution cooled 0.3 g of fine crystals separated. They were recrystallized from alcohol (the substance is sparingly soluble in hot alcohol), and they then melted at 170-173°. A mixture test with the substance of m.p. 174-175° obtained by reaction between 2,5-dimethylthiophene and 3-(chloromethyl)-2,5-dimethylthiophene in presence of aluminum chloride showed no depression in melting point.

	Found %:	C	66.35; 66.68;	H	6.57; 6.69	
$C_{20}H_{24}S_2$.	Calculated %:	C	66.66;	H	6.67	

In another experiment carried out under the same conditions we succeeded in isolating not only the above-described product, but also a small amount of a substance of m.p. 48°, which melted without depression when mixed with the substance of m.p. 48-48.5° isolated in the condensation reaction between 2,5-dimethylthiophene and 3-(chloromethyl)-2,5-dimethylthiophene.

8. Preparation of Substituted Methylenedithiophenes by the Friedel-Crafts Method. Aluminum chloride (0.2 g) was added to a mixture of 5.1 g of 2,5-dimethylthiophene, 7.3 g of 3-(chloromethyl)-2,5-dimethylthiophene, and 35 ml of carbon disulfide. The mixture was stirred for three hours at room temperature, and a further 0.3 g of aluminum chloride was added. On the next day the mixture was heated at 40-50° for 30 minutes. When cool, the mixture was decomposed with ice water, the carbon disulfide layer was separated from the aqueous layer, and the aqueous layer was extracted several times with benzene. The combined carbon disulfide and benzene solutions were washed with water and dried over calcium chloride. The solvents were distilled off, and the residue, a solid, was recrystallized from heptane. The crystals obtained (2.8 g) melted at 150-158° (incipient liquefaction began below this temperature). The heptane mother liquor was evaporated to small bulk. When it was cooled, crystals (1.5 g) of m.p. 42-46° separated; when the filtrate was evaporated a further 1.9 g was obtained. The product of m.p. 42-46° was vacuum-distilled; it boiled at 150° (6 mm). After repeated recrystallization from alcohol the distilled product melted at 48-48.5°. The substance was soluble in benzene, acetone, ether, hot alcohol, and hot heptane, but insoluble in water.

	Found %:	C	66.23; 66.41;	H	6.78; 6.82;	S	26.82; 26.85	
$C_{15}H_{18}S_2$.	Calculated %:	C	66.10;	H	6.77;	S	27.1	
	Found:	M	238					
	Calculated:	M	236					

The substance of m.p. 150-158° (2.8 g) (see above) was distilled at a residual pressure of 4 mm; it boiled at 195-207° and rapidly solidified in the side tube of the distilling flask, thus hindering distillation. After recrystallization from heptane the distilled product melted at 174-175° (change began at 172°).

	Found %:	C	66.74; 66.59;	H	6.84; 6.67;	S	26.29; 27.01	
$C_{20}H_{24}S_2$.	Calculated %:	C	66.66;	H	6.67;	S	26.66	
	Found:	M	351					
	Calculated:	M	360					

The substance was soluble in ether and benzene, and it was sparingly soluble in heptane and hot alcohol.

9. Chloromethylation of 2,5-Dimethylthiophene with the aid of Formaldehyde and Concentrated Hydrochloric Acid in presence of Zinc Chloride. Over a period of 15 minutes, 4.5 g of 37% formaldehyde was dropped into an ice-cooled mixture of 11.2 g of 2,5-dimethylthiophene, 5 g of concentrated hydrochloric acid (sp. gr. 1.18), and 10 g of anhydrous zinc chloride;

the mixture was stirred mechanically at the same temperature for 45 minutes and then at 60° for three hours. When the mixture was cool, water, benzene, and ether were added. The organic layer was separated from the aqueous layer, and the latter was extracted several times with ether and benzene. The combined benzene-ether extracts were washed several times with water, and the solvents were distilled off under reduced pressure. The residue, which partially crystallized out, was diluted with a little ether. The part of the reaction product that did not dissolve in the ether was filtered off and washed several times with small amounts of ether (ether filtrate A); 3.1 g of a colorless crystalline substance, m.p. 150-164°, was obtained. After recrystallization from alcohol and then from heptane it melted at 165-170° (change began at 158°). The substance was distilled at a residual pressure of 4 mm; it came over at 205-215° and rapidly solidified in the side tube of the flask. After recrystallization from acetone the distilled product melted at 170-172.5° (incipient liquefaction began at 167°). A mixture with the substance obtained from 2,5-dimethylthiophene and its bischloromethyl derivative melted at 170-174°. Ether was distilled from the ether filtrate (A). The residue was distilled at a residual pressure of 10 mm and gave the following fractions:

Fraction I, b.p. 157-165°; 3.8 g
Fraction II, b.p. 165-240°; 0.45 g
Residue in flask 1.3 g

Fraction I (3.8 g) was redistilled. The product (3.5 g of crystals) came over at 134-135° (4 mm). After recrystallization from heptane it melted at 48.5° and there was no depression in melting point in a mixture test with the product of m.p. 48° isolated in the condensation of 2,5-dimethylthiophene with its mono(chloromethyl) derivative in presence of aluminum chloride.

	Found %:	C	68.03; 68.07;	H	6.99; 6.97;	S	27.11; 27.28
$C_{12}H_{12}S_2$.	Calculated %:	C	68.10;	H	6.77;	S	27.11

10. Condensation of Benzyl Alcohol with 2,5-Dimethylthiophene. A mixture of 25 g of glacial acetic acid and 25 ml of concentrated sulfuric acid was added to an ice-cooled mixture of 5.6 g of 2,5-dimethylthiophene, 11 g of benzyl alcohol, and 50 ml of glacial acetic acid. The mixture was set aside for three days at room temperature and was then poured into ice water. The oil that separated was extracted with benzene. The benzene solution was washed with water, with 5% sodium carbonate solution, and then again with water. The benzene was distilled off, and vacuum distillation of the residue gave:

Fraction I, b.p. 60-120° (10 mm); 9.7 g
Fraction II, b.p. 130-160° (5 mm); 2.4 g
Fraction III, b.p. 160-190° (5 mm); 2.1 g

Fraction III was an immobile oil that partially crystallized out when kept in a refrigerator. The substance was dissolved in hot alcohol, and when the solution was cooled crystals of m.p. 68-69° (incipient melting at 67°) separated. In a mixture test with 3,4-dibenzyl-2,5-dimethylthiophene (see below) there was no depression of melting point.

11. Preparation of 3,4-Dibenzyl-2,5-dimethylthiophene. Anhydrous aluminum chloride (3.2 g) was added in small portions to a stirred ice-cooled solution of 5 g of the bischloromethyl derivative of m.p. 68° in 20 ml of dry benzene. After the addition of 10 ml of benzene, the mixture was set aside at room temperature for several hours and then decomposed with water and hydrochloric acid. The benzene layer was separated, and the aqueous layer was extracted with benzene. The combined benzene solutions were washed with water and with sodium carbonate solution. The benzene was distilled off, and vacuum distillation of the residue - a dark-red liquid - gave:

Fraction I, b.p. 118-120° (5 mm); 0.45 g
Fraction II, b.p. 187-191° (5 mm); 3 g (solid)
Fraction III, b.p. 191-220° (5 mm); a small amount of red oil

Recrystallization of Fraction II from alcohol gave 1.9 g of colorless crystals, m.p. 68-69°, unchanged by further crystallization.

	Found %:	C	82.64; 82.72;	H	6.82; 7.05;	S	11.32; 11.13
$C_{26}H_{26}S$.	Calculated %:	C	82.19;	H	6.85;	S	10.96

12. Chloromethylation of 2,5-Diethylthiophene. A powerful current of hydrogen chloride was passed into a mixture of 34 ml of 38% formaldehyde and 45 ml of concentrated hydrochloric acid until saturation was reached, and 2,5-diethylthiophene (10 g) was then added gradually at 30°. Hydrogen chloride was passed for a further two hours, and the mixture was then diluted with ice water and extracted with ether. The ether extract was washed with water and with a solution of sodium bicarbonate. It was dried over calcium chloride, ether was distilled off, and the residue was distilled at a residual pressure of 9 mm:

Fraction I, b.p. 128-134°; a small amount
Fraction II, b.p. 138-148°; 10.9 g (solid)

Recrystallization of Fraction II from heptane gave 6 g of a substance of m.p. 53°. The mother liquor yielded 2.6 g of a substance of m.p. 52-54°. After repeated recrystallization the melting point of the substance was 53-54°.

		Found %:	C	50.54; 50.67;	H	5.86; 5.75
$C_8H_{10}Cl_2S$.		Calculated %:	C	50.63;	H	5.91

3,4-Bischloromethyl-2,5-diethylthiophene is soluble in benzene and in hot alcohol; it is somewhat more difficultly soluble in heptane.

13. Chloromethylation of 2,4-Di-tert-butylthiophene. A mixture of 40 g of 37% formaldehyde, 20 ml of concentrated hydrochloric acid, and 100 ml of glacial acetic acid was saturated with hydrogen chloride gas, and 25.5 g of 2,5-di-tert-butylthiophene was then added gradually (over a period of 55 minutes) at 50-55°. After one hour at 50-55° and one hour at room temperature, the cooled mixture was poured into ice water. The reaction product separated in the form of crystals (39 g of crude product). The substance was found to be readily soluble in benzene, acetone, heptane, and hot acetic acid. After recrystallization from acetic acid, the substance melted at 86-86.5°. The yield of recrystallized product was 55%.

		Found %:	C	57.48; 57.46;	H	7.29; 7.35
$C_{14}H_{22}Cl_2S$.		Calculated %:	C	57.34;	H	7.51

No other individual products could be isolated in the chloromethylation of 2,5-di-tert-butylthiophene under the conditions described.

14. Reduction of 3,4-Bischloromethyl-2,5-dimethylthiophene. Stannous chloride (50 g) was mixed with 100 ml of acetic acid, and hydrogen chloride was passed to saturation, i.e. until the whole of the stannous chloride went into solution. The solution was filtered, and 10.4 g of the product of m.p. 68° obtained by the chloromethylation of 2,5-dimethylthiophene was added in small portions. The solution became slightly warm and gradually acquired a reddish-brown color. On the next day the mixture was poured into water. The greenish-yellow oil that separated was extracted with ether, and the extract was then shaken with caustic potash solution and with water. The extract was dried over calcium chloride and the ether was distilled off. Vacuum distillation of the residue gave 4.4 g of a substance having b.p. 75-78° (13-14 mm), n_D^{20} 1.5205.

		Found %:	C	68.63; 68.64;	H	8.47; 8.53; S 22.46; 22.76
$C_9H_{12}S$.		Calculated %:	C	68.57;	H	8.57; S 22.85

The product was unaffected by treatment with acetyl chloride in presence of stannic chloride.

15. Chloromethylation of 3,3'-Methylenebis[2,5-dimethylthiophene]. Freshly distilled chloromethyl methyl ether (3 g) was added to a cooled (ice water) solution of 3 g of the substance of m.p. 47-48° prepared by the chloromethylation of 2,5-dimethylthiophene with formaldehyde and hydrochloric acid in presence of zinc chloride. The mixture was heated for two hours in a water bath at 60°, and the crystalline precipitate formed was filtered off and washed with acetic acid. The crude product (4 g) melted at 167-169° (incipient melting at 155°). After being recrystallized from heptane the substance melted at 172.5-173°.

		Found %:	C	54.31; 54.48;	H	5.26; 5.37
$C_{15}H_{20}S_2Cl_2$.		Calculated %:	C	54.05;	H	5.40

16. Reduction of Bis(2,5-dimethyl-3-thienyl) Ketone. The following compounds were prepared by Buu-Hoï and Nghyen Hoan's method: the acid (VII), m.p. 116-117° (from aqueous alcohol); the acid chloride (VIII), b.p. 103-105° (12 mm); and the ketone (IX), m.p. 63-64° (from alcohol). The ketone

(IX) was synthesized also by Hartough and Kosak's method [12], namely by the action of phosphoric oxide on a mixture of the acid (VII) and 2,5-dimethylthiophene; the ketone obtained again melted at 63°. In the paper referred to above [11] the following constants are given: for the acid (VII) m.p. 117-118°, for the acid chloride (VIII) b.p. 144-145° (13 mm), and for the ketone (IX) m.p. 79°.

The 2,5-dimethylthiophene that we used for the synthesis of the ketone was prepared from 2-methylthiophene by King and Nord's method [5]. The sample so obtained was distilled through a 17-plate column and had b.p. 136.5° (754 mm), n_D^{20} 1.5134, and d_4^{20} 0.9880.

In another experiment on the preparation of the ketone we took 2,5-dimethylthiophene that had been synthesized from 2,5-hexanedione and distilled through a 17-plate column (it had b.p. 136.9° (760 mm), n_D^{20} 1.5127, and d_4^{20} 0.9859). The bis(2,5-dimethyl-3-thienyl) ketone prepared from this material again melted at 63-63.5°.

	Found %:	C	62.11; 62.19;	H	5.66; 5.65;	S	25.51; 25.59
$C_{13}H_{14}OS_2$.	Calculated %:	C	62.40;	H	5.60;	S	25.60

Hydrazine hydrate (100%, 2.7 ml) was added to a mixture of 3.7 g of the ketone and 30 ml of diethylene glycol contained in a three-necked flask fitted with stirrer, reflux condenser, and thermometer. After 25 minutes at room temperature 3 g of caustic potash was added to the mixture, which was then heated for about one hour in a metal bath at 133-134°. A condenser set for distillation was then attached to the flask, and heating was continued until the temperature reached 195° (about two hours). The mixture was maintained at this temperature for three hours. When cool, it was diluted with ice water. The solid that then separated was filtered off, washed with water, and dried. Vacuum distillation of this gave 1.5 g of crystals, b.p. 172° (13 mm). Recrystallization of the product from alcohol gave 1.1 g of m.p. 47-48°, unaffected by repeated crystallization from alcohol. A mixture test of this substance with the substance of the same composition (m.p. 48°) obtained in a different way (see the first scheme, above) showed no depression in melting point.

SUMMARY

1. A study was made of the chloromethylation of 2,5-dimethylthiophene with a mixture of formaldehyde and hydrochloric acid and with chloromethyl methyl ether. The presence of the compound of m.p. 72° described by Buu-Hoi and Hoan could not be detected among the reaction products.

2. In the chloromethylation of 2,5-dimethylthiophene in presence of zinc chloride, compounds were formed which corresponded in composition to 3,3'-methylenebis[2,5-dimethylthiophene] and 3,4-bis(2,5-dimethyl-3--thenyl)-2,5-dimethylthiophene. These compounds were obtained also when 2,5-dimethylthiophene reacted with 3-(chloromethyl)-2,5-dimethylthiophene in presence of aluminum chloride and when 2,5-dimethylthiophene reacted with 2,5-dimethyl-3-thiophenemethanol in presence of sulfuric acid.

3. The compound of m.p. 48.5° was obtained also by the reduction of bis(2,5-dimethyl-3-thienyl) ketone.

4. By the chloromethylation of 2,5-diethylthiophene and of 2,5-di-tert-butylthiophene under selected conditions, the corresponding dialkylbischloromethylthiophenes were obtained. The formation of substituted methylenedithiophenes was not observed under these conditions.

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BRIEF COMMUNICATIONS

ION EXCHANGE ON CELLULOSE AND ITS DERIVATIVES

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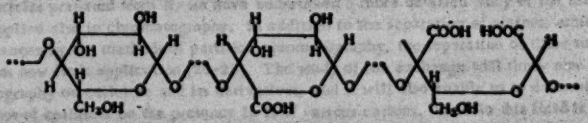
Celluloses, natural and isolated from plant tissues, are able to absorb cations from solutions of neutral salts. Various authors [1-3] have shown that, when cellulose is immersed in a salt solution, the solution becomes acid. Ion exchange on cellulose is now acquiring great theoretical and practical importance. Little progress has yet been made in the elucidation of the source of the exchange properties of cellulose. Some authors [4, 5] consider that ion exchange on cellulose results from the presence of inorganic substances (ash). Others [6, 7] consider that it results from the presence of noncellulosic components (pectic substances, etc.). It is coming to be considered that the exchange properties of cellulose are properties of the cellulose itself, and on this basis investigations are being made of celluloses that are free from inorganic cations and are capable of ion exchange. In a series of investigations it was shown [8] that the ion-exchange properties are dependent on the acidic nature of the cellulose; the authors consider that the acidic properties of cellulose may be intensified in the process of isolation from natural materials.

Sookne and Harris [9] investigated various samples of cotton cellulose, which were freed from inorganic substances or from pectic materials. Their investigations showed that, apart from the COOH groups belonging to pectic substances, cellulose itself contains COOH groups. They found that the exchange capacity of cellulose freed from inorganic substances was 0.066 mg.equiv./g, the capacity of cellulose freed from pectic substances was 0.011 mg.equiv./g, whereas the capacity of the original cellulose was 0.046 mg.equiv./g. Exchange attributable to cations of inorganic substances did not exceed 0.004 mg.equiv./g. Other authors [10, 11] state that COOH groups in oxidized celluloses react with multivalent cations with formation of salts of "cellulose acid". A series of papers [12-14] refer to the ion-exchange properties of oxidized celluloses. The availability of more precise chemical methods now enable the COOH content of cellulose to be determined. It has been found that the COOH content of cellulose prepared according to Corey and Gray is 0.004 mg.equiv./g, that of medicinal cotton wool is 0.02 mg.equiv./g [8], and that of sulfate cellulose is 0.072 mg.equiv./g [7].

No cellulose has yet been isolated which does not contain COOH groups. Analysis of the purest celluloses has shown that they contain 2-3 COOH groups per 1000 glucose residues [15]. If the COOH groups were to be found only in the residues of substances accompanying cellulose, as some authors think [6, 7], then they could not be concerned in the rapid change in the rate of the depolymerization of cellulose that occurs during the first few minutes of its treatment with acid solutions. It is therefore considered that these functional groups belong to particular units of the cellulose macromolecule. This can be expressed diagrammatically by the following formula [16]:



The dots indicate unchanged glucose residues (anhydro-D-glycose).

It has not been found possible to establish whether or not COOH groups are present in the molecule of cellulose before its isolation from the plant. Cellulose with which we have to deal in practice, and also cellulose intended for precise chemical investigations, will always contain functional groups other than OH groups and terminal CHO groups. The presence of COOH groups, even in very small amount, has a great effect on the properties of cellulose and of articles prepared from it. The question of the ash obtained from cellulosic materials is important, for the presence of inorganic substances affects the viscosity, insulation properties, dyeability, etc., of cellulose [5, 6]. On the basis of this it may be supposed that ion exchange on cellulose free from inorganic ion-exchange cations occurs as a result of the presence of COOH groups. With the object of elucidating this matter we have begun an investigation on the ion-exchange properties of cotton cellulose and oxidized celluloses having various COOH contents. The COOH contents were determined by the calcium acetate method [17-19].

The solutions selected for trial were 0.005 M $NiCl_2$ and 0.005 M $FeCl_3$. The solutions were passed through a column of cellulose (as cationite) at 3 ml per sq.cm per minute, the height of the column being 100 mm and its diameter 10 mm. The total exchange capacity was determined from the difference in cation concentration between the ingoing solution and the effluent. The process was continued until the cation concentration in the effluent was equal to that in the ingoing solution. The effluent was collected in 25 ml portions. The absorption of Ni^{2+} was carried out from a solution of pH 6.6, and that of Fe^{3+} was carried out from a solution of pH 1.4. In both cases absorption attained the value of the total exchange capacity. The experimental results for the absorption of Ni^{2+} and Fe^{3+} by cellulose and oxidized celluloses are given in the table, the values given being the means of groups of several determinations.

TABLE

Absorption of Ni^{2+} and Fe^{3+} by Cotton Cellulose and Oxidized Celluloses

Cellulose preparation	COOH content (mg.equiv./100 g of sample	Absorption of	
		Ni^{2+} (mg.equiv./100 g of sample)	Fe^{3+} (mg.equiv./100 g of sample)
Cotton cellulose	1.5	1.3	50
Oxidized cellulose			
1	56	53	43
2	220	200	58
3	280	215	46

As will be seen from the table, the absorption of Ni^{2+} from neutral solution can be correlated with the COOH content of the sample. The behavior of Fe^{3+} is quite different: the absorption is approximately the same for all of the samples, being about 50 mg.equiv./100 g. It follows that the absorption of Fe^{3+} by cellulose has a different mechanism than that of Ni^{2+}. The difference in the behavior of Fe^{3+} is of general interest in relation to the elucidation of the mechanism by which metal hydroxides are absorbed by cellulose.

Since ion exchange on cellulose occurs in many processes and affects the properties of cellulose and of articles prepared from it, we have undertaken a more detailed study of the matter. Cellulose is extensively applied also in chromatography. In addition to the separation of amines, amino acids, and other organic substances by the methods of partition chromatography, the separation of these substances by ion-exchange methods now finds application [20-23]. The study of ion exchange will throw new light on problems in chromatography on cellulose and its derivatives, and it will also enable us to determine the dependence of the properties of cellulose on the presence in it of various cations. Work in this field is continuing.

SUMMARY

1. Ion exchange on cellulose free from inorganic ion-exchange cations is the result of the presence of COOH groups.

2. The mechanism of the absorption of Fe^{3+} ions by cellulose is different from that of the absorption of Ni^{2+} ions.

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ORGANOBORON COMPOUNDS

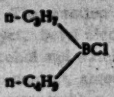
COMMUNICATION 9. ACTION OF PHOSPHORUS PENTACHLORIDE ON DIALKYLBORINIC AND ALKANEBORONIC ESTERS. SYNTHESIS OF DIALKYLCHLOROBORINES AND ALKANECHLOROBORONIC ESTERS

B. M. Mikhailov and T. A. Shchegoleva

Dialkylborinic esters react with phosphorus pentachloride with formation of dialkylchloroborines (dialkylborinic chlorides), alkyl halides, and phosphoryl chloride:

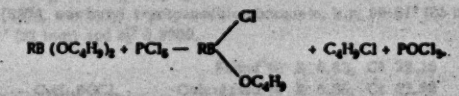
$$RR'BOC_4H_9 + PCl_5 \rightarrow RR'BCl + C_4H_9Cl + POCl_3.$$

By this method butyl dibutylborinate was converted into dibutylchloroborine $(C_4H_9)_2BCl$, and butyl butylpropylborinate was converted into chlorobutylpropylborine:



Dibutylchloroborine has been prepared previously by the action of hydrogen chloride on tributylborine [1]. Compounds of this type containing two different alkyl radicals have not been described previously.

Alkaneboronic esters react equally smoothly with phosphorus pentachloride, and, when one equivalent of phosphorus pentachloride is used, alkanechloroboronic esters are obtained in accordance with the equation:



In this way we prepared butyl esters of 1-butanechloroboronic and 1-propanechloroboronic acids, these being the first representatives of a new type of compounds in which boron is attached simultaneously with an alkyl group, an alkoxy group, and a chlorine atom.

EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere.

Dibutylchloroborine. Phosphorus pentachloride (17.6 g) was added in portions to butyl dibutylborinate (16.8 g) contained in a three-necked flask fitted with an entry tube for nitrogen and a reflux condenser. When the exothennic reaction was complete, butyl chloride and phosphoryl chloride were distilled off under reduced pressure and were collected in a receiver cooled with solid carbon dioxide. The residue was then distilled and yielded 12 g (89%) of dibutylchloroborine, b.p. 58-60° (12 mm). After redistillation the substance boiled at

59.5-60° (12 mm) and 172-174° (atmospheric pressure). The literature [1] gives b.p. 173° and d_4^{20} 0.8590. The substance bursts into flame in the air.

Found %: B 6.75; Cl 22.53
$C_5H_{12}BCl_2$. Calculated %: B 6.74; Cl 22.09

The butyl chloride and phosphoryl chloride were also isolated.

Butylchloropropylborine. The procedure was similar to that of the preceding experiment. Reaction was between 13.3 g of butyl butylpropylborinate [2] and 15 g of phosphorus pentachloride. The product, amounting to 5.1 g (50%), was butylchloropropylborine, b.p. 57-61° (28 mm). After being redistilled it had b.p. 60-61° (28 mm) and d_4^{20} 0.8503. The substance bursts into flame in the air.

Found %: B 7.27; Cl 24.55
$C_5H_{12}BCl_2$. Calculated %: B 7.39; Cl 24.21

The butyl chloride and phosphoryl chloride were also isolated.

Butyl 1-Butanechloroboronate. The procedure was similar to that of the preceding experiment. Reaction was between 20.2 g of dibutyl 1-butaneboronate and 19.6 g of phosphorus pentachloride. The product, amounting to 12.8 g (78%), was butyl 1-butanechloroboronate, b.p. 68-70° (13 mm). After being redistilled it boiled at 64-65° (10 mm) and had d_4^{20} 0.9025.

Found %: B 6.27; Cl 20.03
$C_8H_{18}BOCl$. Calculated %: B 6.13; Cl 20.09

In addition, 8.5 g of butyl chloride and 8.7 g of phosphoryl chloride were isolated.

Dibutyl 1-Propaneboronate. An ethereal solution of propylmagnesium chloride prepared from 36 g of magnesium, 116 g of propyl chloride, and 600 ml of ether was added at −70° to a solution of 160 g of trimethyl borate in 400 ml of ether. The reaction mixture was decomposed with 10% hydrochloric acid, and solvent was distilled from the ether layer. Butyl alcohol (400 ml) was added to the residue. Distillation removed the azeotropic mixture of butyl alcohol and water and then the remainder of the butyl alcohol, and the residue was then fractionally distilled. The product, amount to 132 g (44%), was dibutyl 1-propaneboronate, b.p. 86-90° (10 mm). After being redistilled the ester had b.p. 82-83° (7 mm) and d_4^{20} 0.8152.

Found %: B 5.57
$C_{11}H_{25}BO_2$. Calculated %: B 5.41

Butyl 1-Propanechloroboronate. The procedure was similar to that of the first experiment. Reaction was between 20.7 g of dibutyl 1-propaneboronate and 21.5 g of phosphorus pentachloride. The product, amounting to 14 g (83%), was butyl 1-propanechloroboronate, b.p. 59-67° (25 mm). After being redistilled it had b.p. 60.6-61° (22 mm) and d_4^{20} 0.8999.

Found %: B 6.83; Cl 22.15
$C_7H_{16}BOCl$. Calculated %: B 6.66; Cl 21.82

The butyl chloride and phosphoryl chloride were also isolated.

SUMMARY

1. Dialkylborinic esters react with phosphorus pentachloride with formation of dialkylchloroborines.

2. Alkaneboronic esters react with phosphorus pentachloride with formation of alkanechloroboronic esters.

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TERTIARY ALKYL FLUORIDES AND ALKYLENE DIFLUORIDES IN ORGANOMAGNESIUM SYNTHESIS

A. D. Petrov, V. L. Sushchinsky, and M. P. Shebanova

It is known that alkyl fluorides either do not form Grignard reagents or form them in negligible yield, even if very severe conditions are used [1]. We recently condensed tertiary mono- and di-chloro compounds with halogen compounds of the allyl halide type in presence of magnesium, following Yarovsky's method [2]. We showed that, under the given conditions, even halogen compounds that were unable to form Grignard reagents owing to peculiarities in the structure of their radicals entered into the condensation reaction with formation of olefins, although the yields were generally low. Taking into consideration the fact that the C–F bond energy (102 cal/mole) is considerably higher than the C–Cl bond energy (77.9 cal/mole), we decided to study the condensation reaction of tertiary alkyl fluorides and alkylene difluorides whose chlorine analogs had already been investigated. The results, which are shown in Table 1, indicate that our calculations were justified and that the replacement of chlorine by fluorine in alkyl and alkylene chlorides raises the yield by a factor of 2.5-3. Reaction with the monofluoro compounds was carried out in boiling ether, and reaction with difluoro compounds was carried out at −30°. In view of the high mobility of fluorine in alkyl fluorides [3], the fluoro compounds were prepared from olefins (and diolefins) and hydrogen fluoride at low temperature (−20 to −30°) and were not distilled, being used in the condensation with allyl halides in admixture with the original hydrocarbons.

The properties of the hydrocarbons obtained, together with values from the literature for comparison, are given in Table 2. It is interesting to note that high yields of hydrocarbons containing two quaternary carbons were attained as a result of the high energy of the C–F bond, which enabled the condensation reaction to be carried out rapidly both at +40° and at −30°. It is interesting to note also that, as a side reaction, diolefins are formed from difluoro compounds just as they are from dichloro compounds (this reaction was carried out at −20°) and from dibromo compounds (reaction proceeded only at +35°). In the last case it was not the dibromo compound that reacted, but a monobromo compound that had undergone allyl rearrangement.

EXPERIMENTAL

The hydrofluorination of the olefins (and diolefins) was carried out in a copper reactor fitted with stirrer, thermometer, and copper reflux condenser, through the upper open end of which dry ice and acetone were added. The reactor was placed in a cooling mixture maintained at −40°. Liquid anhydrous hydrogen fluoride was poured into the cooled reactor. The olefin (or diolefin) was then introduced from a dropping funnel and then through the condenser at such a rate that the temperature of the reaction mixture did not exceed −30° (the temperature in the condenser jacket was kept at −25°). When reaction was complete, the excess of hydrogen fluoride was removed with a current of nitrogen at 0-10°. Analysis for fluorine showed that the yields of tertiary monofluoro compounds varied from 30 to 60% and the yield of the difluoro compound was 22%. A difluoro compound was obtained from the diolefin corresponding to the pinacol from the branched ketone isobutyl methyl ketone in a yield of only 10%, but the corresponding dichloro compound could not be obtained at all. The undistilled fluoro compounds in admixture with the original hydrocarbons and the second component of the synthesis was added to magnesium in ether under the usual conditions of the Yarovsky procedure at the temperatures indicated above. The reaction products were decomposed in the usual way and then fractionated. The diolefin (VI) was oxidized with 3% potassium permanganate, and formic acid and 3,4-diethyl-3,4-dimethylhexanedioic acid were identified among the products.

TABLE 1

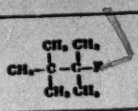
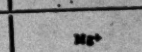
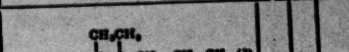
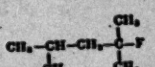
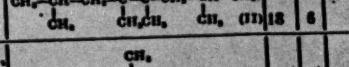
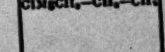
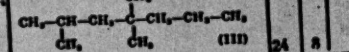
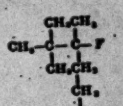
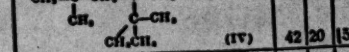
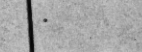
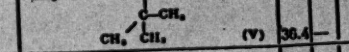
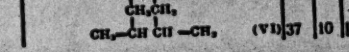
Formula of alkyl or alkylene fluoride	Reagent	Reaction product	Yield (%)	Yield on halogen-containing cpd. %	Lit. reference
		 (I)	10.3	4.5	[4]
	Mg	 (II)	18	8	
		 (III)	24	8	
	Mg +	 (IV)	42	20	[5]
		 (V)	36.4	—	
		 (VI)	37	10	[6]

TABLE 2

Hydrocarbon	Found		Calculated		Properties			B.p. (°C) (p in mm)
	% C	% H	% C	% H	Literature reference	n_D^{20}	d_4^{20}	
(I)	85.76	14.43	85.62	14.38	156.3 (745) 157.5—158.5	1.4311 1.4308	0.7708 0.7711	[4]
(II)	84.90	15.01	84.84	15.16	218 (750)	1.4406	0.7904	
(III)	—	—	—	—	151 (745) 151—152	1.4156 1.4143	0.7360 0.7348	[7]
(IV)	85.73	14.40	85.62	14.38	81 (9) 72—73 (6)	1.4526 1.4528	0.806 0.8055	[5]
(V)	85.21	14.51	85.62	14.38	175 (750)	1.4388	0.7698	
(VI)	88.23	14.04	86.6	13.4	146 (145) 210 (760)	1.4625 1.4620	0.8205 0.818	[6]

Found %: Ag 48.08; C 62.46; H 10.25

$C_{12}H_{23}O_6$. Calculated %: Ag 48.64; C 62.61; H 9.57

The properties of 3,4-dibromo-3,4-dimethylhexane, obtained by the action of HBr on the corresponding diolefin were: b.p. 85-87° (5 mm); n_D^{20} 1.5060; d_4^{20} 1.387.

Found %: Br 58.76; C 36.60; H 6.98

$C_8H_{16}Br_2$. Calculated %: Br 58.82; C 35.04; H 5.84

When the condensation product obtained from this dibromo compound and excess of allyl chloride was fractionated, only a diolefin of composition $C_{11}H_{20}$ was isolated; b.p. 176-178° (750 mm); n_D^{20} 1.4530; d_4^{20} 0.8002.

Found %: C 86.47; H 13.17

$C_{11}H_{20}$. Calculated %: C 86.84; H 13.16

The following substances were identified among the oxidation products of this hydrocarbon: 2-butanone, formic acid, and 2-methyllevulinic acid. This shows that the diolefin is 4,5,6-trimethyl-1,5-octadiene, which has been prepared previously [6].

SUMMARY

It was shown that, when chlorine is replaced by fluorine in tertiary alkyl halides and alkylene dihalides, the yield in the condensation of these substances with Grignard reagents is increased by a factor of 2.5-3.

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* T.p. = C. B. Translation pagination.

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RAPID NONIONIC METATHETIC REACTIONS IN A NONAQUEOUS MEDIUM

Yu. M. Kessler

In the course of a study of the physicochemical properties of solutions of mercury and tin halides in benzene and in nitrobenzene we found that halogen exchange occurred between $Hg(Hal)_2$ and SnI_4 (Hal = Cl, Br) in the solutions $Hg(Hal)_2 - SnI_4 -$ solvent with formation of HgI_2. This reaction occurred when the solid salt $Hg(Hal)_2$ was added to a benzene or nitrobenzene solution of SnI_4 at room temperature. The mixture was shaken, and as soon as most of the $Hg(Hal)_2$ had dissolved, fine yellow crystals began to form throughout the whole solution and were precipitated. The crystals gradually became red in color (in about one hour). The precipitate was identified as HgI_2 by analysis and by the occurrence of a transformation at 127° [1, 2]. The amount of precipitate formed corresponded to the amount of HgI_2 formed by the reaction.

$$SnI_4 + 2Hg(Hal)_2 \rightarrow Sn(Hal)_4 + 2HgI_2 \qquad (1)$$

allowance being made for the solubility of HgI_2 under the given conditions.

A study of the kinetics of the evaporation of solvent from solutions of $HgCl_2$, $HgBr_2$, HgI_2, and SnI_4 in benzene showed that these solutions conform to Raoult's law right up to the saturation point and that, when saturation is reached, the halides crystallize without solvent.* Conductivity measurements on these solutions showed that they have the same conductivity as pure benzene ($\chi < 10^{-8}$ ohm^{-1}cm^{-1}), and it was shown that the same applied to solutions of the type $Hg(Hal)_2 - SnI_4 - C_6H_6$ (after the precipitate had formed) and $HgI_2 - SnI_4 - C_6H_6$.

The literature indicates that with nitrobenzene mercuric chloride forms an incongruently melting compound [4], whereas mercuric bromide [4] and iodide [2] form simple eutectics. There are no data for stannic chloride. We have shown that these halides form conducting solutions in nitrobenzene, the specific conductance in 0.1 mole percent solution at 30° being: $HgCl_2 - 2.0 \cdot 10^{-6}$; $HgBr_2 - 1.2 \cdot 10^{-6}$; $HgI_2 - 1.2 \cdot 10^{-6}$; and $SnI_4 - 4.3 \cdot 10^{-5}$ (ohm^{-1}cm^{-1}). Addition of mercuric iodide to an SnI_4 solution increases its conductivity, which reaches a maximum value of $1.3 \cdot 10^{-4}$ ohm^{-1}cm^{-1} at a molar ratio $HgI_2 : SnI_4$ of 0.1 and is almost unaffected by further increase in the ratio. As HgI_2 is added, the color of the solution changes from deep crimson to pink. Addition of $HgCl_2$ or $HgBr_2$ to $SnI_4 - C_6H_5NO_2$ solutions alters their conductivities (measured after the precipitation of HgI_2) to the corresponding values for the solutions $HgI_2 - SnI_4 - C_6H_5NO_2$.

The color of a nitrobenzene solution of SnI_4 changes reversibly from dark crimson to reddish orange when the temperature is raised to 60-70°, and its conductivity rises until saturation is reached (at 30°). When the solution $HgI_2 - SnI_4 - C_6H_5NO_2$ was electrolyzed (p.d. across cell 5 v, current 10^{-4} amp), a compact layer of HgI_2 was formed on the anode and the liquid near to the cathode acquired a reddish-violet color. These results indicate the occurrence of complex formation in the solution.

In spite of the great difference in the properties of the benzene and nitrobenzene solutions, the apparent courses of the mercuric iodide precipitation reactions are the same in both solvents. This probably indicates that the molecular interaction in nitrobenzene is insufficient to have an appreciable effect on the properties of the halide molecules that determine the course of the reaction. It is notable that the rate of reaction is of the same order as that of ion-exchange reactions, in spite of the complete absence of ions in the benzene solu-

* By means of ebullioscopic measurements, Walden [3] showed that a benzene solution of SnI_4 in benzene has van't Hoff factor $i = 1$.

tions (conductivity data) and of I^- ions in nitrobenzene solutions (electrolysis data). This is especially notable when it is considered that even the isotopic exchange $Br_2^* \rightleftharpoons HgBr_2$ (in carbon disulfide) requires 2.5 minutes [5], though it is true that the iodine in SnI_4 is considerably more mobile, the exchange $I_2^* \rightleftharpoons SnI_4$ in CCl_4 at 0° requiring less than 7 seconds [6]. The only reactions that we know which somewhat resemble those now under consideration are those resulting in the formation of $GeClBr_2I$ and $GeCl_2BrI$ in $GeCl_4 - GeBr_4 - GeI_4$ mixtures, the existence of these compounds being established by a Raman-spectrum study of the mixtures [7], and also that leading to the formation of $SnCl_2I_2$ according to the equation

$$SnCl_4 + SnI_4 \rightleftharpoons 2SnCl_2I_2, \qquad (2)$$

the formation of this compound in an $SnCl_4 - SnI_4$ mixture being established by cryoscopic and ebullioscopic measurements [8]. An attempt to isolate $SnCl_2I_2$ by cooling the mixture or evaporating admixed solvent was not successful [8]. Taking this work into consideration, we may suppose that in our case reaction does not proceed in accordance with Equation 1, its actual course being represented by the equation:

$$SnI_4 + Hg(Hal)_2 \rightarrow Sn(Hal)_2I_2 + HgI_2. \qquad (3)$$

It will be obvious that calculations of the amount of precipitate from Equation 1 and from Equation 3 will give identical results, since the stoichiometric coefficients of $Hg(Hal)_2$ and HgI_2 are equal in both cases.

The precipitation of mercuric iodide as a yellow modification that is unstable at room temperature can be related to the structure of its molecule and the structures of the two modifications. Mercuric iodide molecules are linear (in the vapor). In crystals of the red modification, each mercury atom is surrounded tetrahedrally by four iodine atoms [9]. The yellow modification crystallizes in the $HgBr_2$ structure, in which there are linear $HgBr_2$ molecules and each mercury atom has two bromine atoms as closest neighbors and four more at a greater distance, forming altogether a highly distorted octahedron; the respective distances in the yellow modification of HgI_2 are 2.62 and 3.46 A [10]. It may be supposed that the crystallization of the unstable yellow modification from solution is associated with the tendency to preserve the linear configuration of HgI_2 molecules. We may point out that, when HgI_2 that has been heated above the transition temperature is cooled in the air, the yellow modification can be preserved at room temperature for more than one hour without its being converted into the stable modification (according to our own experiments).

Owing to the absence of the necessary thermochemical data, we were unable to estimate the heats of the reactions under discussion. The existing data are, however, sufficient to show that the reactions must be appreciably exothermic.

In conclusion we may state our opinion that the reactions described, being examples of very rapid reactions, present considerable interest for the theory of the transition state (see e.g. [11]) and also from the point of view of their molecular mechanism. We plan to carry out thermochemical and kinetic studies of these reactions.

The author expresses his great indebtedness to A. F. Kapustinsky for valuable suggestions made during the discussion of this work.

SUMMARY

1. Studies were made of the electrical conductivities of ternary mixture of $Hg(Hal)_2$ (Hal = Cl, Br), SnI_4, and benzene or nitrobenzene and of the kinetics of evaporation of solvent from the binary mixtures $Hg(Hal)_2$ — benzene and SnI_4 — benzene.

2. It was shown that in $Hg(Hal)_2 - SnI_4$ — solvent mixtures, instantaneous halogen exchange occurs with formation of HgI_2.

3. It was shown that this exchange is not associated with the presence of ions or stable complexes in the solutions and does not depend on the difference in properties between the solvents used.

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REACTION OF DEUTERIUM ATOMS WITH ALKENES

DEPENDENCE OF THE EXTENT OF THE DEUTERATION OF METHANE ON THE CONCENTRATION OF DEUTERIUM ATOMS IN THE SYSTEM

R. E. Mardaleishvili, G. B. Parilsky, V. A. Poltorak, and V. V. Voevodsky

In the foreign literature it is considered that there is general agreement on the correctness of the view that the formation of highly deuterated products by reaction between deuterium atoms and molecules and various organic compounds is the result of an exchange reaction occurring between free radicals formed under the given conditions and deuterium atoms [1, 2]. For methyl radicals, for example, the exchange is generally expressed as follows:

$$\left.\begin{aligned} \dot{C}H_3 + D &\rightleftharpoons \dot{C}H_2D + H \\ \dot{C}H_2D + D &\rightleftharpoons \dot{C}HD_2 + H \end{aligned}\right\} \quad (1)$$

and so on.

In our first investigation [3] we established that exchange between radicals and deuterium, at least when the radicals are generated by interaction between alkenes and hydrogen (H or D) atoms formed by the dissociation of hydrogen (H_2 or D_2) in a discharge tube, involves deuterium molecules, not deuterium atoms. Hence, in the exchange reaction of methyl radicals which we have taken as an example, the process must be expressed as follows:

$$\left.\begin{aligned} \dot{C}H_3 + D_2 &\rightleftarrows H-\overset{\displaystyle H}{\underset{\displaystyle H-D}{\overset{|}{\underset{|}{C}}}}-D \rightleftarrows \dot{C}H_2D + HD \\ \dot{C}H_2D + D_2 &\rightleftarrows D-\overset{\displaystyle H}{\underset{\displaystyle H-D}{\overset{|}{\underset{|}{C}}}}-D \rightleftarrows \dot{C}D_2H + HD \end{aligned}\right\} \quad (2)$$

Owing to the high velocity with which processes of the type (2) occur, the phenomenon of exchange can be applied as a new method for the identification of free radicals. For example, this method has been applied [4, 5] in demonstrating that some free radicals undergo isomerization with migration of the free valency:

$$\text{—}\dot{C}H\text{—}CH_2\text{—}CH_2\text{—} \rightleftharpoons \text{—}CH_2\text{—}CH_2\text{—}\dot{C}H\text{—} \qquad (3)$$

In particular, it was shown in this investigation that extensive exchange with the reaction products is observed even when radicals are generated in the system [(H + H_2 + Ar) + alkene] + D_2 (i.e. when the alkene is admixed with the stream before the admixture of deuterium). Under these conditions the formation of deuterium atoms by the reaction

$$H + D_2 \rightleftharpoons HD + D \qquad (4)$$

cannot occur, for hydrogen atoms are absent at the point at which deuterium is added to the stream because of the occurrence of the reactions

$$H + \text{alkene} \longrightarrow \dot{R}$$

$$H + \dot{R} \longrightarrow \dot{R}_1 + \dot{R}_2;$$

$$H + H + M \longrightarrow H_2 + M^*;$$

in which substantially the whole of the hydrogen atoms are consumed. This result confirms the conclusion reached previously, namely, that the exchange of the hydrogen atoms of radicals for deuterium is the result of reaction between these radicals and deuterium molecules [3].

The present investigation had the object of studying the part played by deuterium atoms in the deuteration of the products and it has not only given results that are of interest on their own account, but has provided new data in confirmation of the occurrence of exchange between radicals and D_2 molecules. We considered it to be especially desirable to give these data in the present paper because Steacie [2], in an examination of the results of our first investigation in his recently published extensive monograph, expressed doubts, for which he gave no grounds, with regard to the feasibility of the exchange mechanism that we suggested.

EXPERIMENTAL

1. In planning this investigation we considered that a study of the dependence of the yield and extent of deuteration of the products on the concentration of D atoms would enable us to establish, first, the part played by D atoms in the formation of and exchange with particular radicals and, second, the part played by D atoms and by various radicals formed by their aid in the formation and deuteration of the products. With this in view, we investigated the deuteration of methane formed in (D + D_2) + alkene systems (the alkene being C_2H_4, C_3H_6, or i-C_4H_8) at various concentrations of deuterium atoms and particularly at [D] $\longrightarrow$ 0.

Let us examine the question of the deuteration of methane formed at extremely low concentrations of deuterium atoms, since this procedure enables us to decide which of the two exchange mechanisms — atomic or molecular — should be used in the analysis of the results obtained in experiments at high concentrations of D atoms. The deuteration of methane at [D] $\longrightarrow$ 0 must proceed differently according as exchange with free radicals occurs predominantly in interaction with atoms or with molecules of deuterium. In both cases the extent of the deuteration of methane can be calculated.

a) (α_{D_M})$_{[D]\to 0}$ — in accordance with the atomic exchange scheme. The most probable mechanism of methane formation, e.g. in the system (D + D_2) + C_2H_4, under our experimental conditions (pressure in the gas stream about 1 mm, t = 20-25°) is as follows:

$$\begin{aligned}
&0.\quad D + C_2H_4 \rightarrow CH_2D - \dot{C}H_2\\
&1.\quad CH_2D - \dot{C}H_2 + D \rightarrow 2\,\dot{C}H_2D\\
&2.\quad \dot{C}H_2D + CH_2D - \dot{C}H_2 \rightarrow \begin{cases} {}^{1}/_{2}\{CH_2D_2 + CH_2 = CH_2\} \\ {}^{1}/_{2}\{CH_3D + CHD = CH_2\} \end{cases}
\end{aligned} \qquad (5)$$

The reactions

$$3.\ \dot{C}H_2D + D + M \rightarrow CH_2D_2 + M^*$$
$$4.\ \dot{C}H_2D + D_2 \rightarrow CH_2D_2 + D,$$

by which methane can also be formed, are unable to compete with reaction (5, 2): reaction (5, 3) cannot compete because of the insignificant concentration of D atoms in the system (for $[D] \rightarrow 0$) and the need for three-body collisions, and reaction (5, 4) cannot compete because of the activation energy required (8 kcal; $E_2 \approx 0$). These reactions, therefore, need not be taken into consideration. We do not take account also of the possibility of the isotope-exchange reaction

$$\dot{C}H_2D + D \rightleftarrows \dot{C}HD_2 + H,$$

since at $[D] \rightarrow 0$ it cannot occur at an appreciable rate owing to the fact that, under these conditions, almost all of the D atoms are used up in the reaction (5, 0).

It may be considered, therefore, that methane is formed exclusively by reaction (5, 2), and the extent of its deuteration should not then exceed

$$(\%\,D_M)_{[D]\rightarrow 0} = \frac{{}^1/_3 \times 2 + {}^2/_3 \times 1}{4} \times 100 = 33\%$$

b) $(\%\,D_M)_{[D]\rightarrow 0}$ — in accordance with the molecular exchange scheme. In this case the mechanism of the formation of $\dot{C}H_2D$ radicals is the same as that given above. Owing to the presence in the system of D_2 molecules in large excess over the amount of methyl radicals, the latter undergo exchange until an equilibrium mixture of radicals

$$\dot{C}D_3 + \dot{C}D_2H + \dot{C}HD_2 + \dot{C}H_2D,$$

is formed which we shall denote by $C\mathcal{D}_3$. Similar exchange will be undergone by other radicals formed in the system, for example

$$CH_2D—\dot{C}H_2 \xrightarrow{D_2} CH_2D—C\mathcal{D}_2.$$

Disproportionation of deuterated methyl radicals by a reaction of the type (5, 2), i.e. in the present case the reaction

$$C\mathcal{D}_2 + CH_2D—C\mathcal{D}_2 \rightarrow \begin{matrix} {}^2/_3 \\ {}^1/_3 \end{matrix} \left\{ \begin{matrix} C\mathcal{D}_2D + CH_2 = C\mathcal{D}_2 \\ C\mathcal{D}_2H + CHD = C\mathcal{D}_2 \end{matrix} \right\} \qquad (5, 2')$$

leads to the formation of methane, for which the extent of deuteration can be calculated from the extent of deuteration of methyl radicals ($\%\,D_{C\mathcal{D}_3}$) and $\%\,D$ — the composition of the heavy hydrogen passed through the discharge

$$(\%\ D_M)_{[D]\to 0} = {}^3/_4(\%\ D_{C_2D_6}) + {}^1/_4 \cdot {}^1/_3 \cdot (\%\ D). \qquad (6)$$

In our experiments a mixture of hydrogen and deuterium containing 96.5% of the latter was passed through the discharge tube, so that

$$\%\ D = 96.5\% \text{ and } D_{C_2D_6} \approx (0.965)^6 \cdot 100 \approx 90.$$

Substituting these values in Equation 6 we obtain

$$(\%\ D_M)_{[D]\to 0} = 75.5\%$$

So that according to the atomic exchange scheme the deuteration of methane formed in the system $(D + D_2) + C_2H_4$ at $[D] \to 0$ should not proceed to an extent of more than 33%, whereas according to the molecular exchange scheme it can attain 75.5%.

In experiments with isobutene and propene the extent of the deuteration of methane should differ from the values calculated by either scheme owing to the fact that it is determined by the probability of the saturation of the methyl radical by a D atom of the isobutyl or propyl radical, respectively. However, in all three cases the extent of the exchange of methyl radicals (i.e. $\%D_{CD_3}$) must be the same — 33%, according to the atomic exchange scheme and 90% according to the molecular exchange scheme.

2. A diagram of the apparatus used in these experiments is given in Fig. 1. Beyond the zone of the electrical discharge, alkene was admixed to the stream of partially dissociated deuterium. The mixture of gases together with reaction products was then passed through one of five traps 6-10 cooled with liquid nitrogen, these being connected in parallel and provided with taps. In each of these traps condensable products were frozen out; these products were formed by the action of deuterium atoms, the concentration of which was determined by the magnitude of the discharge current ($[D] \approx \sqrt{I}$ [6]).

The stream of gases that did not condense at the temperature of liquid nitrogen (methane + deuterium) then passed through one of the five traps 1-5, which were similar to those described above, but were filled with activated charcoal. The whole of the methane and much of the deuterium were in this way removed from the stream. The use of this system of traps enabled us to obtain five test samples of the reaction products in one experiment, so that the question of nonreproducibility of results from one experiment to another did not arise.

Before an experiment, the apparatus and traps were evacuated to a pressure of 10^{-6} mm, and degassing of the charcoal was effected by heating the quartz traps 1-5 with the flame of hand gas blowpipe. All the taps were then closed, and the tap a was turned into the position A in order to evacuate the discharge tube and the reaction vessel while bypassing the traps. A stream of hydrogen was then passed periodically through the discharge tube and the discharge was switched on at a current of 400-500 ma. This resulted in the heating of the electrodes, which facilitated complete removal of possible contamination from them. This degassing of the electrodes was carried out several times, the discharge being finally produced in deuterium. Before passage into the discharge tube, the deuterium was passed through a trap cooled with liquid nitrogen in order to remove vapors of grease and mercury.

After the establishment of the deuterium stream, the alkene (ethylene, propene, or isobutene) supply was turned on,* and the current in the discharge was maintained at a definite value, controlled by potential difference across the electrodes. After 2-3 minutes first taps 1 and 6 and then taps 1' and 6' were opened. Immediately afterwards, tap a was turned from the position A (evacuation of the tube) to position B (evacuation of traps). The stream of gases then passed through the trap 6, through the trap 1, and then through the tap a to the pumps.

* Deuterium and alkene were added at constant rate through the calibrated capillaries K_D and K_{RH} (Fig. 1).

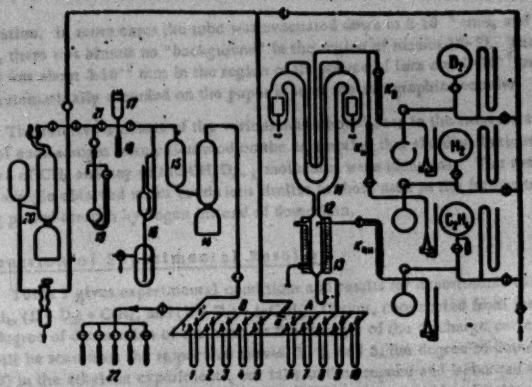


Fig. 1. Diagram of apparatus for the study of reactions in the system $(D + D_2)$ + alkene: 1-10– traps with taps 1,1'–10,10'; 11– discharge tube; 12– reaction vessel with electric furnace 13; 14– mercury diffusion pump for pumping gases from traps into the flask 15; 16– McLeod gage; 17– LT- lamp manometer; 18– side tube for the freezing-out of gases; 19– manometer; 20– mercury diffusion pump with trap and fore-vacuum flask; 21– vacuum taps; 22– "rake" for the transference of gas samples to the mass spectrometer for analysis; K_D, K_H, and K_{RH}– calibrated capillaries for the delivery of gas from the respective flasks.

Reaction proceeded for two minutes, the condensable products being trapped in trap 6, and methane and deuterium (D_2 + HD + H_2) in trap 1. The tap 3 was then turned into position A, and tap 6 was closed. After 30 seconds taps 1 and 1' were closed and taps 2 and 7 were opened. The desirable current strength was established in the discharge and at the end of the third minute the operations described were repeated in traps 2 and 7, and so on.

The heavy hydrogen passing into the discharge tube in our experiments contained 96.5% deuterium. The current passed in the discharge was varied from 20 to 500 ma. The pressure of the gases in the stream was about 1 mm.

3. The separation of methane–deuterium mixtures adsorbed on charcoal was carried out by pumping off the deuterium with the diffusion pump 14 into the flask 15, from which it could be removed further with the aid of the pump 20. In order to follow the course of the pumping of deuterium into the flask 15, the LT-2 lamp manometer 17 was fused on and the variation of pressure was recorded with the autographic recorder EPP-09. The separation of deuterium was considered to be complete when, after a preliminary thawing of the charcoal trap and refreezing with liquid nitrogen,* there was a rise in pressure in the flask 15 (the tap 21 being open) in the next 10-15 minutes. The pure methane remaining in each trap was desorbed at room temperature and then transferred by adsorption on charcoal at –196° into one of the branches of the detachable "rake" 22. The rake with its samples of methane was transferred to the mass spectrometer, on which it was analyzed for isotopic composition.

5. The mass spectra of deuteromethanes were determined on an MS-4 apparatus at an emission current of 2 ma and an ionizing p.d. of 70 v. Before the measurements the tube was carefully degassed by long heating and

* The taps on the traps were of course closed during these operations.

evacuation. In some cases the tube was evacuated down to $8 \cdot 10^{-8}$ mm, and in others to $1 - 1.2 \cdot 10^{-7}$ mm. As a result, there was almost no "background" in the region of masses 12-21. The gas pressure during the measurements was about $3 \cdot 10^{-3}$ mm in the region of the source of ions and $2 \cdot 10^{-2}$ mm in the tube. The mass spectra were automatically recorded on the paper tape of the autographic recorder.

The relative amounts of the various deuteromethanes in the mixture and the average degree of deuteration of each sample were calculated on the assumption that the distributions of the corresponding peaks in the spectra of CH_4 and any of the CH_xD_{4-x} molecules were identical. The mass spectrum of CH_4 was determined for a sample obtained under conditions similar to those used in the formation of deuteromethanes, the discharge being passed through hydrogen instead of deuterium.

Discussion of Experimental Results

Table 1 gives experimental conditions and results for experiments carried out in the systems $(D + D_2) + C_2H_4$, $(D + D_2) + C_3H_6$, and $(D + D_2) + i\text{-}C_4H_8$. Curves, constructed from these data, showing the dependence of the degree of deuteration of methane on the strength of the discharge current (i.e. on $[D]^2$) are given in Fig. 2. As will be seen from the respective curves, 1, 2, and 3, the degree of deuteration of methane rises with increase in [D] in the ethylene experiments, but falls in the propene and isobutene experiments. The cause of this behavior in the relationship between $\%\ D_M$ and [D] will be considered below, and we shall now consider the values of the degree of deuteration of methane at $[D] \to 0$, as found by extrapolation of the curves 1, 2, and 3 to their intersection with the axis of ordinates. Extrapolation of Curve 1, which corresponds to the system $(D + D_2) + C_2H_4$, gives a value of 73.7 for $(\%\ D_M)\ [D] \to 0$.

TABLE 1

Degree of Deuteration of Methane formed in the System $(D + D_2) +$ + RH at Different Concentrations of D Atoms

System	Temperature (°C)	Current (ma)	Ratio $[D_2]:[RH]$	Degree of deuteration of methane ($\%\ D_M$)
$(D + D_2) + C_2H_4$ . . .	25	50	50 : 4	74.5
	25	100	50 : 4	75.0
	25	200	50 : 4	76.5
	25	300	50 : 4	78.0
	25	500	50 : 4	81.5
$(D + D_2) + C_3H_6$ . . .	25	25	50 : 4	78.1
	25	50	50 : 4	77.3
	25	125	50 : 4	74.6
$(D + D_2) + i\text{-}C_4H_8$ . .	25	25	50 : 4	89.5
	25	75	50 : 4	89.2
	25	200	50 : 4	88.9
	25	275	50 : 4	88.6

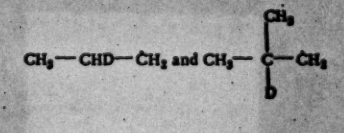
The experimentally observed degree of deuteration of methane is considerably higher than that calculated (33%) in accordance with the scheme of exchange between methyl radicals and D atoms, but it is in close accord with value of 75.5% calculated according to the molecular exchange scheme. We reach the same conclusion when we compare calculated and experimental values of the degree of deuteration of methane formed in experiments with propene and isobutene (Table 2).

Let us examine this question in greater detail. As we have pointed out above, if we assume a mechanism of the formation of methane by reactions of the type (5, 0-2), the extent of its deuteration can be determined by the equation

$$(\%\ D_M)_{[D] \to 0} = \tfrac{3}{4}\ (\%\ D_{C_xH_y}) + \tfrac{1}{4} \cdot \beta \cdot \%\ D,$$

in which $\%\ D_{C_xH_y} = (0.965)^3 \cdot 100 = 0.90$, and $\%\ D = 96.5$.

With the aid of the values of $(\%\ D_M)_{[D] \to 0}$ in Experiments 2 and 3 we may determine the probability β of the saturation of methyl radicals with D atoms. The relevant calculation gives $\beta_2 = 0.5$ in the experiment with propene and $\beta_3 = 1$ in the experiment with isobutene. This implies that the saturation of methyl radicals in these experiments proceeds by disproportionation with the respective radicals



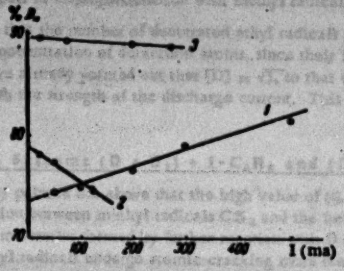


Fig. 2 Curve for the degree of deuteration of methane formed in the system (D + D_2) + alkene as a function of the concentration of D atoms in the system: 1—(D + D_2) + C_2H_4; 2—(D + D_2) + + C_3H_6; 3—(D + D_2) + i-C_4H_8.

These results are in agreement with those of our previous investigation [4, 5], in which it was shown that in the addition of deuterium (or hydrogen) atoms to isobutene both tert-butyl and isobutyl radicals are formed and that isobutyl radicals enter the disproportionation reaction with transfer of the D (or H) atom at the tertiary carbon atom with greater ease than tert-butyl radicals. We must point out that in the calculation of the probability β we used the value of the extent of exchange of methyl radicals obtained in accordance with the molecular exchange scheme. Calculation in accordance with the atomic exchange scheme gives values of β of greater than unity (β_2 = 2.1 and β_3 = = 2.7) which is absurd. These results confirm the fact that we established previously, namely, that exchange with the free radicals is effected with the participation of deuterium molecules, not atoms.

We shall now examine the question of the degree of deuteration of methane as a function of the concentration of D atoms.

TABLE 2

Calculated and Experimental Values of the Degree of Deuteration of Methane formed in the System (D + D_2) + Alkene (% D = 96.5)

Experiment No.	System	Isotopic Composition of methane	$(\%D_M)_{[D]\to 0}$ according to the atomic exchange scheme	$(\%D_M)_{[D]\to 0}$ according to molecular exchange scheme	$(\%D_M)_{[D]\to 0}$ found by experiment
1	(D + D_2) + C_2H_4	$C\mathcal{D}_3$ ($^1/_3$D + $^2/_3$H)	32	75.5	73.7
2	(D + D_2) + C_3H_6	$C\mathcal{D}_3$ ($^1/_3$D + $^1/_3$H)	38	79.5	79.8
3	(D + D_2) + i-C_4H_8	$C\mathcal{D}_3$D	48	91.5	89.6

Reaction in the System (D + D_2) + C_2H_4

According to the reaction (5, 2°), in disproportionation between methyl and ethyl radicals, molecules of deuterated ethylene are formed as well as methane. With increase in the concentration of D atoms in the system, it becomes increasingly probable that the ethylene molecules will again react with D atoms with formation of ethyl radicals of, for example, the following isotopic composition:

$$1.\ CHD = C\mathcal{D}_2 + D \rightarrow CHD_2 - \dot{C}\mathcal{D}_2. \qquad (7)$$

$$2.\ CHD = C\mathcal{D}_2 + D \rightarrow \dot{C}HD - C\mathcal{D}_2D \xrightarrow[\text{exchange}]{D_2} \dot{C}\mathcal{D}_2 - C\mathcal{D}_2D.$$

It is quite to be expected that disproportionation between methyl radicals and such deuterated ethyl radicals will give more highly deuterated methane

$$\dot{C}\mathcal{D}_3 + CD_2H - \dot{C}\mathcal{D}_2 \rightarrow \begin{matrix} {}^2/_3 \\ {}^1/_3 \end{matrix} \begin{cases} C\mathcal{D}_3D + CHD = C\mathcal{D}_3 \\ C\mathcal{D}_3H + CD_2 = C\mathcal{D}_3 \end{cases} \qquad (8)$$

as in this case CD_3D molecules will be formed with a probability of 2/3, not 1/3 as in reaction (5, 2'). Finally, disproportionation with $CD_3D-\dot{C}D_2$ radicals must give CD_3D and CD_4 molecules exclusively.

Hence, the cause of the increase in the degree of deuteration of methane formed in the system $(D + D_2) + C_2H_6$ with increase in the concentration of D atoms is to be found in the increase in the number of deuterated ethyl radicals taking part in disproportionation with methyl radicals.

It will be clear that the number of deuterated ethyl radicals taking part in reaction (8) will be proportional to the square of the concentration of deuterium atoms, since their formation by reactions (5, 0) and (7) requires two D atoms. We have already pointed out that $[D] \approx \sqrt{I}$, so that the "supplementary" deuteration of methane must vary linearly with the strength of the discharge current. This is actually observed experimentally (Curve 1, Fig. 2).

Reactions in the Systems $(D + D_2) + i\text{-}C_4H_8$ and $(D + D_2) + C_3H_6$

We have already pointed out above that the high value of $(\%\ D_M)_{I\to 0}$ in the reaction with isobutene is due to disproportionation between methyl radicals CD_3 and the isobutyl radicals formed together tert-butyl radicals. The isobutene molecules formed by further reaction with D atoms again give radicals of two types. On the other hand, isobutyl radicals undergo atomic cracking more readily than tert-butyl radicals [4, 5]. As a result of these circumstances, with increase in the concentration of D atoms in the system the ratio of the amounts of tert-butyl and isobutyl radicals rises sharply. At the same time it becomes more probable that the reaction

$$1.\ \dot{C}D_3 + CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}D-\dot{C}H_2 \rightarrow CD_3D + \text{isobutene}$$

will meet competition from the reaction

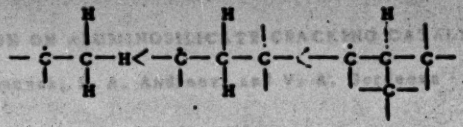
$$2.\ \dot{C}D_3 + CH_3-\underset{\displaystyle CH_3}{\overset{|}{\dot{C}}}-CH_2D \rightarrow \begin{matrix} {}^1/_9\{ & CD_3D + i\text{-}C_4H_8 & \} \\ {}^8/_9\{ & CD_3H + i\text{-}C_4H_7D & \} \end{matrix} \qquad (9)$$

The latter process results in the formation of CD_3H molecules with a probability of 8/9 and of CD_3D molecules with a probability of only 1/9, whereas in the reaction (9, 1) only CD_3D molecules will be formed. This, in our opinion, is the cause of the fall in the degree of deuteration of methane formed in the system $(D + D_2) + i\text{-}C_4H_8$ with increase in the concentration of D atoms (Curve 3, Fig. 2). It should be noted that in the experiments with ethylene the fall in the degree of deuteration is linear with respect to I, i.e. depends on $[D]^2$. The fall in the degree of deuteration of methane is much steeper in the reaction with propene (Curve 2, Fig. 2), which may readily be explained when we consider that in this case with increase in the concentration of deuterium atoms the competition of two reactions occurs:

$$\begin{matrix} 1.\ \dot{C}D_3 + CH_3-CHD-\dot{C}H_2 \rightarrow & {}^1/_3\{ & CD_3D + \text{propene} & \} \\ & {}^2/_3\{ & CD_3H + \text{propene} & \} \\ 2.\ \dot{C}D_3 + CH_3-\dot{C}H-CH_2D \rightarrow & {}^1/_6\{ & CD_3D + C_3H_6 & \} \\ & {}^5/_6\{ & CD_3H + C_3H_5D & \} \end{matrix} \qquad (10)$$

It follows from the difference in the slopes of Curves 2 and 3 that in the propene experiment the contribution of reaction (10, 2) in the formation of methane is considerably greater than that of the analogous reaction (9, 2) in the isobutene experiment. In our opinion this must be attributed to the fact that in the disproportionation reaction with methyl radicals the primary hydrogen atoms (H or D) in isopropyl radicals can compete more readily with secondary H or D atoms in propyl radicals than primary and tertiary H or D atoms can in isobutyl

and tert-butyl radicals respectively. From this we may draw the very reasonable conclusion that the mobility of hydrogen atoms (H or D) attached to α-carbon atoms in radicals increases in the series:



SUMMARY

1. The present investigation, which differs from our previous investigations in that the mass-spectrometric method of analysis was used, provides quantitative data that confirm the correctness of the mechanism that we have proposed, according to which exchange occurs between free radicals and molecular deuterium. It is shown that deuterium atoms do not play an appreciable part in the process of exchange with free radicals.

2. Our previous conclusion - that in the addition of hydrogen atoms (H or D) to alkenes, radicals of both possible types are formed - is confirmed.

3. It is shown that the main reaction resulting in the formation of methane from methyl radicals at low temperature is one of disproportionation with larger radicals.

4. It is shown that, in disproportion reactions with other radicals, the mobility of the hydrogen atom (H or D) attached to the α-carbon of the radical increases as we move from a primary to a tertiary atom.

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COKE FORMATION ON ALUMINOSILICATE CRACKING CATALYSTS

B. V. Klimenok, E. A. Andreev, and V. A. Gordeeva

Carbonaceous deposits formed on catalysts in high-temperature reactions are generally regarded as products of undesired side reactions that accompany the main reaction. For a long time the same view was held with respect to the "coke" - carbonaceous and resinous deposits - formed on aluminosilicate catalysts in the cracking of hydrocarbons. The investigations of Frost [1], Thomas [2], and others have shown that coke, though reducting the activity of an aluminosilicate catalyst, nevertheless plays an important, positive role in catalytic cracking, being a hydrogen donor that can bring about the saturation of unsaturated catalytic-cracking products.

The nature of coke is still obscure. Apart from the short paper by Thomas [2], no studies of the nature of coke have appeared in the literature. It must be pointed out that, even then, this single investigation by Thomas suffers from substantial methodological defects that lower the value of the experimental results. The main fault lies in the fact that reversibly adsorbed cracking products were not removed from the catalyst surface. In the combustion of the coke, these reversibly adsorbed hydrocarbons also underwent combustion. The determination of the composition of the coke was therefore not reliable. It is doubtful whether the empirical formula found for the coke ($CH_{1.31}$) represented its true composition; it should have been poorer in hydrogen. After extraction of soluble substances in benzene, the coke was found to be still richer in hydrogen ($CH_{1.42}$).

With the object of studying the nature of coke and the part it plays in the process of catalytic cracking, we carried out investigations in the following directions: 1) improvement of the method of determining the amount and composition of the coke; 2) determination of the relationship between the composition of the coke and the duration of cracking; and 3) investigation of the degree of unsaturation of the coke.

EXPERIMENTAL

Improvement of the Method of Determining the Amount and Composition of the Coke

Coke is now generally analyzed by combustion in air and absorption of carbon dioxide and moisture with suitable substances. Before the combustion the carbonized catalyst is treated in a stream of pure nitrogen for some time, this being supposed to remove all of the reversibly adsorbed hydrocarbons. Experiment shows, however, that blowing-out with nitrogen does not remove them completely. Thus, when hot carbonized catalyst is blown out with nitrogen for 0.5-1 hour and the system is then connected to an oil pump and evacuated through a trap cooled with liquid air, a certain amount of liquid hydrocarbons always collects in the trap. For example, in one experiment (No. 64), after 30 ml of carbonized catalyst had been blown out for 30 minutes with nitrogen, 0.02 g of liquid hydrocarbons was extracted from it by evacuation. It will be clear that the combustion of these adsorbed hydrocarbons together with the coke would yield incorrect results for the amount and composition of the coke. The error resulting from the combustion of 0.02 g of liquid hydrocarbons can be estimated roughly. In the same experiment, after the blowing and evacuation the amount and composition of the coke was determined:

Amount of coke ..... 30.9 mg
Composition of coke ..... $CH_{0.88}$

Hence, if the catalyst had not been evacuated, the amount of coke determined by combustion would have been 30.9 + 20 = 50.9 mg, i.e. 65% greater than the actual value; the composition would have been expressed by the formula $CH_{1.97}$ (it is assumed that the liquid hydrocarbons removed by the pump were olefins C_nH_{2n}). This was confirmed also by direct comparison of determinations on the coke with and without the evacuation (Table 1). The experiments were carried out under identical conditions.

TABLE 1

Experiment 64	Amount of coke (mg)	Composition of coke
With evacuation	30.9	$CH_{0.48}$
Without evacuation	51.1	$CH_{1.12}$

TABLE 2

Carbon in the form					Total carbon (mg)
CO_2		CO			
(mg)	(%)	(mg)	(%)		
5.1	52	4.6	48		9.7
22	84.6	4.0	15.4		26
42	75	14	25		56
92	84.3	17	15.7		109

It is clear from these results that the determination of the actual composition and amount of the coke demands a more careful removal of reversibly adsorbed hydrocarbons than that which can be achieved by the usual blowing with nitrogen. Evacuation with an oil pump (0.01 mm) at 350-400° removes practically the whole of the reversibly adsorbed hydrocarbons in 10-15 minutes.

It is of no less importance for the determination of the actual composition of the coke to take account of the carbon that is oxidized during the regeneration into CO and is therefore not trapped by the CO_2 absorber. Experiment shows that the percentage content of CO varies greatly according to the experimental conditions. Thus, in Experiment 66 composition and quantity determinations were carried out on equal volumes of catalyst carbonized to different extents. The carbonized catalysts were subjected to evacuation for 20 minutes. The coke was oxidized with air at 550°, the carbon dioxide being absorbed with Ascarite, and the carbon monoxide collected in the exit gases and determined by absorption with ammoniacal cuprous chloride. Table 2 gives the results of the carbon estimations on the coke.

It will be seen from Table 2 that the content of carbon present as CO varies over a wide range (15-48%). An appreciably greater proportion of carbon leaves in the form of CO in the regeneration of weakly carbonized catalysts. In all the succeeding experiments on the nature of the coke, the procedure that we had shown to be essential - evacuation of the catalyst before the combustion of the coke and making allowance for CO in the analysis of the combustion products - was adopted.

Determination of the Relationship between the Composition of the Coke and the Duration of Cracking

The effect of the duration of cracking on the composition of the coke was studied for the case of the cracking of hexane over spherical-grain aluminosilicate catalyst. The duration of cracking was varied from 1.5 to 180 minutes; the temperature of cracking was 520°; the space velocity for the hexane was kept constant at 0.27 $hour^{-1}$ in all experiments; and the amount of catalyst was 30 ml. After the cracking the catalyst was evacuated with an oil pump for 20 minutes at 400°. The analysis of the coke was carried out by the method described above, account being taken of the carbon monoxide formed. Four experiments of duration 1.5, 15, 60, and 180 minutes were carried out. The results of the analysis of the combustion products are given in Table 3.

The composition and the amount of the coke are shown as functions of the duration of cracking in Fig. 1. The number of hydrogen atoms per carbon atom in the coke and the amount of coke (mg) are plotted as ordinates, and the duration of cracking (minutes) as abscissae. It will be seen from Fig. 1 that, with increase in the duration of cracking, the coke becomes poorer in hydrogen and this impoverishment

TABLE 3

Duration of cracking (minutes)	Weight of absorbed H_2O (mg)	Weight of absorbed CO_2 (mg)	Volume CO collected (ml at STP)
1.5	11.7	18.3	8.7
15	19.2	80.1	7.5
60	24.9	154.7	26
180	39.3	354.7	32

TABLE 4

Duration of cracking (minutes)	Weight of hydrogen in coke (mg)	Weight of carbon in coke (mg)	Weight of coke (mg)	Composition of coke
1.5	1.3	9.7	11.0	$CH_{1.61}$
15	2.13	26	28.1	$CH_{0.98}$
60	2.77	56	58.8	$CH_{0.59}$
180	4.37	109	113.4	$CH_{0.48}$

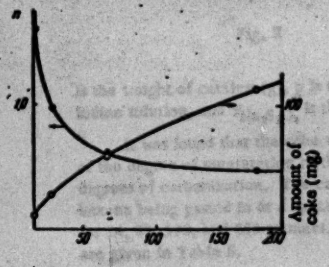

Fig. 1.

proceeds particularly rapidly at the beginning of the cracking. In the course of the first hour the atomic ratio of hydrogen to carbon is reduced by a factor of almost three (from 1.6 to 0.6), whereas in the course of the next two hours it is reduced by a factor of only 1.25 (from 0.6 to 0.48).

Investigation of the Degree of Unsaturation of the Coke

Experiments on the cracking of hexane and isooctane with participation of radioactive ethane, ethylene, and propene labeled with the carbon isotope C^{14} indicates that the coke is formed mainly from olefins [3]. It is possible that the formation of coke on a catalyst begins with the polymerization of olefins and the formation of polyolefins as a result of the partial decomposition of the polymers[4]. In this case the coke, particularly when "young", should possess some unsaturation.

With the object of determining the degree of unsaturation of the coke, a method was developed for the determination of its iodine value (grams of iodine required to saturate 100 g of coke). The carbonized catalyst (10-20 g) was ground in an iron mortar to 0.5-0.3 mm grains. It was found to be best to sieve out the larger and the finer particles. The ground catalyst was placed in a flask, and a titrated iodine solution was added until a thin slurry was obtained. The flask was closed with a glass stopper and placed in the dark for ten minutes. Distilled water (200 ml) was then added, and iodine was titrated as usual with thiosulfate, it being preferable to add starch before the end of the titration. As the suspension was dark in color, some experience is necessary in order to detect the disappearance of the blue color of the starch. The blue color is most readily seen in the upper layers of the suspension after it has been allowed to stand for 10-20 seconds. Also, at the end point the suspension loses its relative stability and begins to precipitate appreciably more rapidly after being shaken. It is necessary simultaneously to carry out a similar titration of the same amount of fresh catalyst (control experiment) in order to take account of adsorption of iodine by the aluminosilicate. The amount of iodine required is generally only a small fraction of the amount absorbed by the coke.

In order to calculate the iodine value of the coke it is necessary to determine the coke content (% by weight) of the catalyst on another sample of the same portion of carbonized catalyst. The iodine value was calculated from the formula:

$$I = \frac{10{,}000\,[a \cdot T_{I_2} - (b_1 - b_2)T_{Na_2S_2O_3}]}{cp},$$

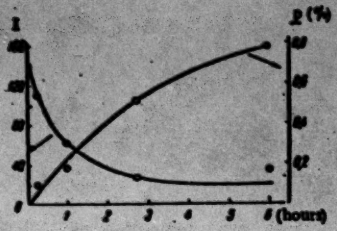

Fig. 2

TABLE 5

Duration of cracking (minutes)	Coke content of catalyst (% by weight)	Weight of coke (g)	Iodine value of coke
14	0.106	0.0235	110
60	0.189	0.0425	62
162	0.516	0.117	38
360	0.781	0.169	34.5

in which a is the volume of iodine solution (ml), b_0 is the volume of thiosulfate solution (ml) required in the control experiment, b_1 is the volume of thiosulfate solution (ml) required in the titration of the coke, c is the weight of catalyst (g), p is the coke content of the catalyst (% by weight), T_{I_2} is the titre of the alcoholic iodine solution, and $T_{Na_2S_2O_3}$ is the iodine titre of the thiosulfate solution.

It was found that the coke was indeed more or less unsaturated. In order to determine the dependence of the degree of unsaturation of the coke on its "age", several samples of catalysts were prepared with different degrees of carbonization. The carbonization of the catalysts was carried out by cracking hexane at 520°, the hexane being passed in at a space velocity of 0.275. Four portions of catalyst, each 30 ml, were carbonized for 14, 60, 162, and 360 minutes. The results of the determinations of the amount of coke and its iodine value are given in Table 5.

The dependence of the iodine value of the coke and the degree of carbonization of the catalyst on the duration of cracking is shown in Fig. 2. It can be seen from Fig. 2 and Table 5 that "young" coke has high iodine values of 100 or more, indicating that it has considerable unsaturation. With increase in the duration of catalytic cracking the iodine value of the coke diminishes. The saturation of the coke is particularly rapid in the early period of the catalytic cracking. In the first hour the iodine value of the coke falls from 110 to 60, i.e. by almost 50%. The fall then becomes less marked, and after three hours the iodine value of the coke becomes stabilized at a level of 30-35. Even "old" coke, therefore, has a certain degree of unsaturation, probably attributable to the later deposits. Simultaneously, as can be seen from Fig. 2, the amount of coke increases continuously.

Calculation shows that in a coke of iodine value 110 there is one double bond for about 16 carbon atoms, and in a coke of iodine value 34.5 — one double bond for 53 carbon atoms. Comparison of the iodine values (Table 5) with the compositions (Table 4) of the cokes shows that in catalytic cracking an aliphatic coke ($CH_{1.6}$; I = 110) is formed at first, and this is then gradually converted by condensation into an aromatic coke ($CH_{0.4}$, I = 30).

In order to resolve the question of whether the variation in the degree of unsaturation of the coke with duration of cracking is essentially associated with the cracking process itself, the following experiment was carried out.

The cracking of hexane was carried out over 60 ml of aluminosilicate catalyst for 10 minutes. The cracking temperature was 520°, and the hexane was passed in at a space velocity of 0.275 hours^{-1}. After the cracking the catalyst was evacuated for 20 minutes, removed from the reactor, and halved. The first half was immediately analyzed for coke content and iodine value, and the second half was returned to the reactor and treated with a stream of pure nitrogen at 520° for three hours. The second half of the carbonized catalyst was then analyzed for iodine value and coke content. The results of the determinations are given in Table 6.

The iodine values and coke contents of the two portions of catalyst are the same within the errors of measurement. It may therefore be concluded that heating of the carbonized catalyst for three hours in an inert atmosphere does not affect the iodine value and that the reduction in the degree of unsaturation of the coke under conditions of catalytic cracking, as also the change in the composition of the coke, is

TABLE 6

Catalyst	Coke content of catalyst (% by wt.)	Iodine value of coke
First half	0.092	130.4
Second half	0.105	142
Mean	0.098	136.2

TABLE 7

Portion No.	Space velocity of hexane ($hour^{-1}$)	Coke content of catalyst (% by weight)	Iodine value of coke
1	0.275	0.23	38
2	1.11	0.124	34
3	1.74	0.098	30
		Mean	34

TABLE 8

Duration of cracking (minutes)	Temperature (°C)	Coke content of catalyst (% by weight)	Iodine value of coke
60	460	0.23	38
60	520	0.19	60

associated essentially with the reactions occurring in catalytic cracking over aluminosilicates. The aging of the coke, i.e. the cyclization and condensation of the hydrocarbons of the coke, occurs only to the extent that redistribution of hydrogen occurs in the catalytic cracking.

The effect of the space velocity or contact time on the iodine value of the coke was also studied. Three 30-ml portions of catalyst were carbonized at different space velocities of hexane – 0.273, 1.11, and 1.74. Hexane cracking was carried out at 460° for one hour. The results of determinations of iodine values and coke contents are given in Table 7.

The results in Table 7 show that the degree of unsaturation of the coke does not greatly depend on the space velocity at which the starting material is passed in. For an increase in the space velocity from 0.275 to 1.74, i.e. by a factor of more than six, the iodine value of the coke fell by only 11%. Such a change is within the limits of the errors of measurement of iodine values for coke.

The effect of temperature on the rate of saturation of the coke can be seen from Table 8.

Both experiments were carried out at the same space velocity of hexane, 0.275 $hour^{-1}$. The amount of catalyst was 30 ml.

It will be seen from Fig. 8 that rise in the temperature of catalytic cracking is accompanied by a rise also in the iodine value of the coke, i.e. the rate of saturation of the coke falls. This accords with the known fact that the content of unsaturated hydrocarbons in cracking products increases with rise in the cracking temperature.

SUMMARY

1. In catalytic cracking the elementary composition of the coke formed changes in the direction of impoverishment in hydrogen as the process proceeds. At the beginning of cracking the composition of the coke can be expressed approximately by the formula $CH_{1.6}$, and when the impoverishment in hydrogen has reached its limit it is expressed by the formula $CH_{0.5}$.

2. The coke always has a definite degree of unsaturation. The earliest coke has an iodine value of 150. Coke saturated to the limit probably has an iodine value of zero. The saturation of the coke is organically associated with the redistribution of hydrogen in the process of catalytic cracking.

3. Change in the space velocity at which the starting material is passed in has almost no effect on the rate of saturation of the coke.

4. With rise of temperature, the rate of saturation of coke in the catalytic cracking process diminishes.

5. A comparative examination of the compositions and iodine values of the cokes shows that in the course of the cracking process the nature of the coke changes. As, in the course of the cracking, hydrogen is given up for the saturation of unsaturated cracking products, so the coke becomes converted into a saturated condensed-aromatic coke.

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DETERMINATION OF π-ELECTRON DENSITY AND INTERATOMIC DISTANCES

COMMUNICATION 3. CONFIRMATION OF THE HYPOTHESIS

G. V. Bykov

Four years ago I published three papers [1-3]* in which it was suggested, first, that the general π-electron cloud (equivalent to n electrons) of a molecule consists of π-electron bond charges such that each separate charge A may have a fractional value when expressed in electronic units,

$$\Sigma A = n; \qquad (1)$$

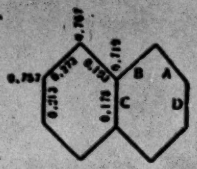
and second, that all bonds formed by atoms that are π-electron donors may posses a certain π-electron charge. Morcover, an equation was proposed which expressed a linear relationship between π-electron charge and bond length, and numerous calculations were made with the aid of this equation.

In the last four years several papers have appeared that are closely allied in subject matter. It was considered desirable to compare the basic theses of these authors and the results of their calculations with mine and to take a brief glance at the future prospects of this line of work.

I

The concept of the π-electron charge of bonds must be distinguished from the concepts of percentage double-bond character and of fractional order of bonds; the latter are theoretical concepts that have no clear physical meaning and they are unable to express the additivity of π-electron charges of bonds. However, to a certain extent they can be regarded as approximations to the concept of π-electron charge. At least, if we avoid the concept of the fractional order of a bond in the form proposed and developed by Coulson [4-6], we can make the transition to the concept of π-electron charges. This transition was made by McWeeny [7], whose investigation, which was of a preliminary nature, was published almost at the same time as our second paper [2]. McWeeny states that in many cases it is preferable to divide the general π-electron charge of the molecule into localized regions, but although this procedure has been "tacitly assumed in certain cases (diatomic molecules), its generality and applicability has apparently not been determined". The total π-electron charge can be distributed between the atoms and bonds – the emphasis is McWeeny's – in such a way that the sum of the individual charges is equal to the total number of π-electrons. McWeeny points out that, unlike bond orders and free valencies, localized charges give an "analytical picture", which he illustrates for the case of naphthalene (see figure). McWeeny points out also the close relationship that must exist between the properties of a bond and its π-electron charge. We can agree with McWeeny's views in the main, but must take exception to his treatment in two respects: working by analogy to Coulson's method, he distributes π-electron charges not only among the bonds, but also among the atoms, and he does not indicate the possibility of a partial distribution of the π-electron charges in C–H bonds.

* We take this opportunity of pointing out some misprints: in [1], p. 393 on the tenth line from the bottom, read δ_{CH_3-C} instead of Δ_{CH_3-C}; in [2], p. 824 on the 27th line from the top, read $CH_3-C^{+\frac{1}{3}}_{-\frac{1}{3}}-CH$ instead of $CH_3-C^{-\frac{1}{3}}_{+\frac{1}{3}}-CH$; in [3], p. 368 on the 30th line from the top, read $\underline{1}_{CO}$ instead of $\underline{1}_{CO_2}$, and p. 371 on the 22nd and 23rd lines from the top, read CO instead of CO^2.



Distribution of the π-electron charges in naphthalene according to McWeeny.

TABLE 1

Distribution of π-Electron Charges in Naphthalene (for lettering of bonds see figure)

Bond	According to the data of			According to Equation 4
	Scherr [8]	Platt [9]	Bagdasaryan [10]	
A	1.078	1.04	1.005	1.19 (1.395) *
B	0.705	0.80	0.825	0.79 (1.425)
C	0.634	0.58	0.53	1.00 (1.393) **
D	0.937	0.98	0.955	0.93 (1.404)

* The interatomic distances are given in parentheses.

** The length of the bond C is not in accord with calculations by the molecular-orbital method (l_{CC}=1.424) and with the lengths of similar bonds in other condensed aromatic compounds; for example, the length of the analogous bond in anthracene is l_{CC}=1.438 and its π-electron charge, according to Equation 4, is A_{CC}= 0.71. To a lesser degree these remarks apply also to the bond A.

On the basis of a free-electron model, Scherr [8] has made calculations for a large group of aromatic hydrocarbons, and also for ethylene, butadiene, and 3-methylene-1, 4-pentadiene; they give values of π-electron charges only for C–C bonds. Unlike McWeeny, Scherr is inclined to identify π-electron charges ("densities") of bonds and the order of a "mobile" (π-electron) bond as understood by Coulson. As will be seen from the discussion above, there is no adequate foundation for this view. Platt [9] constructed a mechanical model for the determination of π-electron charges in aromatic molecules; his results are close to those of Scherr. By applying the quantum-statistical treatment of an electron gas to molecules containing conjugated bonds, Bagdasaryan [10] calculated the π-electron charges ("electron densities") of bonds in a series of hydrocarbons, but, like Scherr, he did not take the π-electron charges of C–H bonds into account.

Table 1 shows the distribution of π-electron charges in naphthalene according to the data of Scherr, Platt, and Bagdasaryan and also our value calculated from Equation 4 (see below) on the basis of Robertson's values for the interatomic distances [11].

In outlining a program of future work in my previous paper [3], I referred to the application of these methods and of the conclusions reached as the result of the calculation of π-electron charges to the study of the σ-electron distribution. However, before I communicated my results,* Sandorfy and Daudel [12] showed the possibility, at least in principle, of calculating σ-electron bond charges by the method of molecular orbitals. According to their calculations, the minimum value of the σ-electron charge of a C–C bond is A^{CC}=1.498 electrons.

It will be seen from these examples that problems relating to the electron charges of bonds are already receiving attention from theoretical chemists, who, unlike me, are approaching the solution of the problems from the point of view of quantum mechanics.

* I made this communication only in June 1955 at the All-Union Conference on Kinetics, Catalysis, and Reactivity in Moscow.

II

There is a large group of bonds in which only one of the two atoms forming the bond is a π-electron donor. It includes the bonds: C–H in acetylene, C–CH_3 in propene, C–Cl in phosgene, C–O in phenol, and C–N in aniline. In the last three compounds chemists assume the existence of a weak π-bond resulting from interaction between the π-electrons of carbon and free electron pairs of the valency shell of the chlorine, oxygen, and tervalent nitrogen atoms. It is from this point of view that explanations are now advanced for the shortening (as compared with a σ-bond) of , for example, the C–Cl bond in aromatic compounds [13] and in phosgene [14].

Such concepts have not been extended to C–C and C–H bonds owing to the absence of free electrons in the valency shells of hydrogen and σ-quadrivalent carbon. However, I have shown [1, 2] that these bonds also must have a certain π-electron charge.* Either indirectly or directly this view is shared by certain other authors. When Shigorin [15] writes that the π-electron of the atom C" in propylene $C'H_2{-}C''H{-}C'''H_3$ moves not only in the field of the atom C', but also in the field of the atom C"', this means that a π-electron-density distribution is created such that a part of it is associated with the bond C"–C"'. At the same time we cannot agree with Shigorin's assertion [16] that when a hydrogen of the methyl group of propene is replaced by halogen there will no longer be any π-electron interaction between the atoms C" and C"'**. A displacement of π-electron density in the C–CH_3 bond of propyne is assumed by B. and A. Pullman, who speak even of the symmetry of the π-electron cloud with respect to this bond [17].

As regards the C–H bond, Myers and Gwinn [18] in their review of the radiospectroscopy of gases indicate some experimental grounds for the view that the C–D bond in deuterochloroacetylene has π-electron character and that the similar shortening of the C–H bond is in accord with its π-electron character. Indirect proof of the distribution of π-electron charges in C–H bonds is provided also by Scherr's calculations, according to which the π-electron charge of the C–C bond of ethylene has the value A_{CC}=1.333 electrons. Where then in ethylene is the remaining 0.667 of a π-electron to be found, and why should not the remaining π-electron cloud in such compounds be oriented along C–H bonds?

We see therefore that more and more arguments are appearing in favor of the view that the π-electron cloud of an atom donor of π-electrons is distributed over all the bonds that it forms.

III

It is extremely probable that the value of the electronic charge of a bond mainly determines the properties of the bond. However, the form of the functional relationship must be determined for each property separately. On the basis of a comparative study of the experimental data, the author [2] concluded that there is a linear relationship between the length of a bond and its π-electron charge:

$$l = L - \Delta A, \qquad (2)$$

in which l is the bond length, L is the length of the standard single bond, A is the π-electron charge of the bond, Δ is the specific contraction (the shortening when A is one π-electron). L and Δ depend on the type of bond. Thus, for the C–C bond Equation 2 has the form:

* Thus, as a rule all bonds for which it is assumed that the percentage double-bond character $p > 0$ or the bond order $R > 1.00$ have a π-electron charge $A > 0$, but the converse is not necessarily true.

** There are other important theses in Shigorin's theoretical treatment, and, in the present author's opinion, whether one agrees with them or not, they should be given very serious consideration. If we consider only the main points, then in my view Shigorin's criticism of the concepts of the electron "doublet" and of "multiple" bonds are correct and timely, but one of his main theses– the hypothesis of the π-like electron– is, to say the least, superfluous: all the facts in the explanation of which it is applied can be explained equally satisfactorily by the character of the distribution of σ- and π-electron density. Another defect of Shigorin's theoretical scheme is its markedly qualitative character, whereas in operating with the concept of the magnitude of the π-electron charge of a bond, one may readily turn to a quantitative treatment of the questions examined by Shigorin.

$$l_{CC} = 1.542 - 0.149\, A_{CC}. \quad (3)$$

so that

$$A_{CC} = \frac{1.542 - l_{CC}}{0.149}. \quad (4)$$

The analogous formula for the C–N bond is:

$$A_{CN} = \frac{1.47 - l_{CN}}{0.1}. \quad (5)$$

Equation 4 was applied in the calculation of the π-electron charges of C–C bonds in various hydrocarbons for the first time. As will be seen from Table 2, the results are in good agreement with the later results of Scherr, Platt, and Bagdasaryan.

TABLE 2

Bond	According to the results of			
	Bykov [2]	Scherr [8]	Platt [9]	Bagdasaryan [10]
C–C in ethylene	1.42	1.333	—	—
C–C (2-3) in butadiene	0.55	0.800 (0.70)*	—	0.65 (0.55)*
C–C (ar-alk) in styrene	—	0.654 (0.60)*	—	0.74 (0.69)*
C–C (ar-alk) in stilbene	0.65	0.682 (0.63)*	0.74	—
C–C (1-1') in biphenyl	0.42	0.515	—	0.73

* In their calculations the authors assume that the π-electron charges associated with C–H bonds are zero, whereas according to my calculations [1] $A_{CH} = 0.1$ electron for the 2- and 3-C–H bonds of butadiene. The calculated values given in the original papers should therefore be reduced by 0.1 approximately for butadiene and by 0.05 approximately for styrene and stilbene.

For the relationship between the calculated values of the π-electron charges ("densities") and the experimentally determined interatomic distances Scherr proposes the following linear equation:

$$r - s\,(A) = 1.665 - 0.1398\,[1 + b\,(rs)], \quad (6)$$

in which $r - s\,(A)$ is the length of the C_r——C_s in angstrom – in our notation l_{CC} – and $b(rs)$ is the π-electron charge ("density") of the same bond – in our notation A_{CC}. Changing the notation and making a suitable transformation, we obtain:

$$l_{CC} = 1.525 - 0.1398\, A_{CC}. \quad (6a)$$

The similarity between Equations 3 and 6a is obvious, but there is a difference between them that is not in favor of Equation 6a, for at $A_{CC} = 0$ the latter equation gives a value of 1.525 A for the length of a single C–C bond, which is not in accord with fact: for diamond values of 1.542 and 1.544 have been found for l_{CC}; in ethane it is 1.535.

For the determination of π-electron charges in polyenes, Scherr proposes the empirical equation:

$$b(rs)\,[=A_{CC}] = 1 - \frac{(-1)^r}{(n+1)\sin\left\{\pi\left(r+\frac{1}{2}\right)\Big/ n+1\right\}}, \qquad (7)$$

in which r is the ordinal number in the chain for the first atom forming the bond and n is the total number of carbon atoms in the polyene. The formula expresses both the alternating effect and the gradual leveling out of the bonds with the lengthening of the chain, but it again does not take the π-electron charges of the C–H bonds into consideration.

Calculations of interatomic distances and π-electron charges of bonds with the aid of Equations 1 and 2 can, as I showed in previous papers [2, 3], be used for the correction of experimental data. In this connection great importance must not, of course, be attached to inferences made regarding the doubtfulness of certain experimental results, such as were made, for example, with respect to the lengths of the C–C and C–O bonds in acetone •, for it is sufficient to make comparisons with homologous and analogous compounds in order to arrive at the same conclusions. Inferences that cannot be made by any other means are of much greater interest. For example, I cast doubt on the experimental data for interatomic distances in allene [2]. It has been found [20] that the shortening of the C–C bond in allene is indeed greater than was supposed: the new value is $l_{CC} = 1.309$, whereas the old was $l_{CC} = 1.330$.

The same calculations can be also of theoretical interest. In the paper [3] I directed attention to the fact that the reduction in the π-electron charge of the C–O bond that is attributable to the participation of the oxygen in a hydrogen bridge gives reason to suppose that the hydrogen bond has a π-electron character. Shortly afterwards, a number of new arguments in favor of this supposition were advanced by Shigorin [12]. Another example: in the compound $(CH_3SO_2)_2CCNCH_3$ Wheatley [22] found the following interatomic distances: $>C\overset{1.542}{\text{———}}C\overset{1.154}{\text{———}}N\overset{1.424}{\text{———}}CH_3$; he concluded that in such compounds interatomic distances do not provide a satisfactory criterion for the assessment of bond order, since it would be necessary to assume the "quinquevalence" of the central carbon atom. Incidently, there is no anomaly here, as will be seen from a calculation of the π-electron charges of the bonds by Equations 4 and 5: $>C\overset{1.94}{\text{———}}C\overset{2.14}{\text{———}}N\overset{0.44}{\text{———}}CH_3$.

To the first approximation, therefore, Equation 2 expresses the relationship between the π-electron charges of the bonds and their lengths, and moreover, the good compatability of the results of calculations by this equation for the electron distribution in hydrocarbons, halogen-, oxygen-, and nitrogen-containing organic compounds, and certain inorganic nitrogen compounds [2, 3] provides weighty arguments in favor of the correctness of the views advanced in Sections I and II.

IV

What changes will be necessary if the above views, which have received confirmation from different directions, become accepted in chemistry? The principle according to which the covalent bond is formed by an integral, generally even, number of electrons, while remaining true to the first approximation, will have to give way to another system of postulates that are more closely in accord with actuality:

1. Covalent bonds vary with respect to the values of their σ- and π-electron charges.

2. The main characteristic of the covalent bond is the value of its σ- and π-electron charge, which is the main factor determining its properties.

3. The mutual effects of atoms are manifested by a certain distribution of σ- and π-electron charges in the bonds, which is the main factor determining the reactivity of the molecule.

4. For the calculation of the distribution of σ- and π-electron charges among bonds — and therefore for the establishment of the relationship between the physical and chemical properties of molecules — from the results of physical methods of investigation, it is possible to find methods of calculation that are cruder than quantum-mechanical methods, but are mathematically simple and universal in application.

• See the partial correction of these results in the paper of Allen et al. [19].

The acceptance of these views will result in substantial reconstruction of the modern electronic theory of molecular structure and reactivity and in re-examination of many of its underlying principles. The importance of this new line of thought must not be underestimated. The examples that we have given show conclusively that it has already begun to assert itself in work representing different lines of approach and carried out in different countries. The number of such examples could probably be increased *. Unfortunately, the individual investigators who are following this new path and are arriving at the same conclusions and even at identical numerical results are not yet coordinating their work together, and authors of reviews on molecular structure and the chemical bond for the most part either do not mention such investigations at all, or do not grasp the main significance of them. Sometimes it must be supposed that this work is deliberately ignored. However, the history of chemistry shows that no new line of thought has yet been welcomed with open arms by its contemporaries.

SUMMARY

1. Covalent bonds in molecules are formed by σ- and π-electron charges, which are not in general equal to a whole number of electrons.

2. All bonds attached to atom donors of π-electrons have π-electron charges.

3. To the first approximation, a linear relationship can be assumed between π-electron charge and bond length.

4. A new and very promising line of work is being developed in the theory of the electronic structure of molecules.

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* The author would be grateful for information on any omissions he may have made, particularly papers published before 1951.

** T. p. = C. B. Translation pagination.

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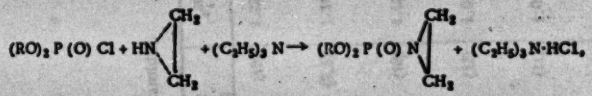
ORGANOPHOSPHORUS ETHYLENIMINE DERIVATIVES

COMMUNICATION 1. REACTION OF ETHYLENIMINE WITH DIALKYL PHOSPHOROCHLORIDATES

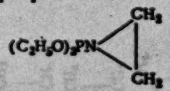
N. P. Grechkin

Organophosphorus ethylenimine derivatives have not yet been investigated systematically, and in the chemical literature there are only sporadic references (almost entirely in patents) to individual compounds [1-8]. It is however quite evident that organophosphorus ethylenimine derivatives are of great interest, both from the point of view of the development of methods of synthesizing organophosphorus compounds and from the point of view of their practical application (which is referred to in a comparatively large number of patents) and of the study of their biological activity.

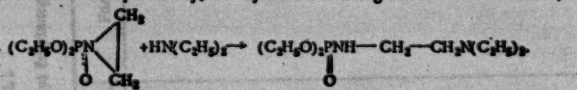
By means of the method suggested by Bestian [1], which consists in the treatment an organophosphorus acid halide with ethylenimine in presence of triethylamine in benzene.



we prepared a series of dialkyl ethylenephosphoramidates [dialkyl P-1-aziridinylphosphonates] of general formula , in which R is an aliphatic radical containing 1-5 carbon atoms. By an analogous reaction we prepared also diethyl ethylenephosphoramidite:



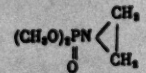
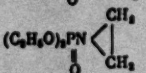
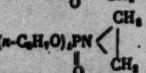
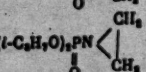
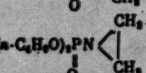
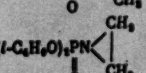
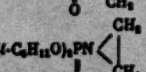
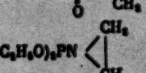
The properties of the compounds obtained are given in Table 1. By making use of the reactivity of the ethylenimine ring, we succeeded in effecting some transformations of the ethylenephosphoramidic esters. When diethyl ethylenephosphoramidate was heated with a large excess of diethylamine in presence of ammonium chloride, the ethylenimine ring was opened with formation of diethyl 2-diethylaminoethylphosphoramidate. An analogous reaction [9] has been studied previously, 2-ethylaziridine being treated with an amine, e.g. morpholine, or ammonia.



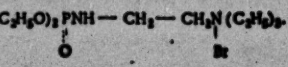
Addition of ethyl bromide to this last compound yielded the ethobromide of diethyl 2-diethylaminoethylphosphoramidate as a readily crystallizing substance:

TABLE 1

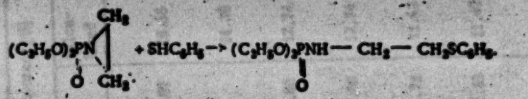
Dialkyl Ethylenephosphoramidates and Diethyl Ethylenephosphoramidite

No.	Formula of substance	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	Phosphorus content (%) found	Phosphorus content (%) calculated	Yield (%)
1		99.5—100 (10)	1.2212	1.4375	32.42	32.67	20.62; 20.30	20.53	73.5
2		108.5 (9.5)	1.1148	1.4362	42.00	41.91	17.45; 17.57	17.31	82
3		127—128 (10)	1.0584	1.4382	51.36	51.15	14.97; 14.88	14.97	76
4		112—113 (12)	1.0439	1.4310	51.33	51.15	15.03; 15.09	14.97	74
5		146—147 (11)	1.0260	1.4407	60.45	60.38	13.39; 13.45	13.19	87.5*
6		135.5—136 (10.5)	1.0174	1.4367	60.48	60.38	13.16; 13.20	13.19	83*
7		155.5—156.5 (10.5)	1.0004	1.4415	69.49	69.67	11.90; 11.85	11.79	81*
8		57.5—58.5 (10)	1.0070	1.4458	43.15	43.13	18.95; 19.01	19.02	63.5

* An excess (about 10%) of triethylamine was taken.

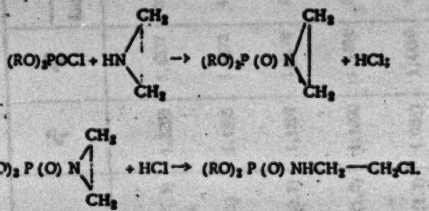


An analogous reaction occurred when diethyl ethylenephosphoramidate was heated with benzenethiol: the ethylenimine ring was opened [10] with formation of diethyl 2-phenylthioethylphosphoramidate:



It must be pointed out that the ethylenimine (aziridine) ring substituted at the nitrogen by the dialkoxyphosphinyl group loses much of its reactivity: thus we were unable to open the ring of the ethylenephosphoramidic esters with phenol, whereas such a reaction has been described for other aziridines [11]. We were equally unsuccessful in our attempts to synthesize P-3-oxazolidinylphosphonic esters by reaction of ethylenephosphoramidic [P-1-aziridinylphosphonic] esters with aldehydes and ketones, although analogous compounds are readily obtained from ethylenimine even under mild conditions [12]. The behavior of ethylenephosphoramidic esters toward some other reagents (alkyl halides, acid halides, and others) was studied.

When dialkyl phosphorochloridates react with ethylenimine in absence of a base, the cyclic amide formed is broken down by hydrogen chloride with formation of dialkyl 2-chloroethylphosphoramidate:



In all, seven of these 2-chloroethylamides were prepared, R being an aliphatic radical having 1-5 carbon atoms. The constants of the compounds obtained are given in Table 2.

An attempt to synthesize diethyl 2-chloroethylphosphoramidite from diethyl phosphorochloridite and ethylenimine was not successful.

EXPERIMENTAL

1. Synthesis of Dialkyl Ethylenephosphoramidates. All of these compounds were prepared under analogous conditions. A solution of 31.4 g (0.157 mole) of dipropyl phosphorochloridate in 50 ml of dry benzene was added dropwise to a solution of 6.75 g (0.157 mole) of ethylenimine and 15.8 g (0.157 mole) of triethylamine in benzene over a period of 40 minutes at a temperature of from − 5° to + 5°. When the whole of the phosphorochloridate had been aded, the cooling bath was removed, and the mixture was stirred for 1.5-2 hours at room temperature. The reaction mixture was then heated for one hour at 40-50°. During the whole of these processes, the reactants were stirred together vigorously by means of a nichrome wire stirrer. The mixture was cooled to room temperature, and the triethylamine hydrochloride was then filtered off, washed twice with dry benzene, dried, and weighed; the yield was 20 g (94%). Benzene was distilled from the filtrate under reduced pressure. Two fractionations of the residue from an Arbuzov flask gave pure Substance 3 (Table 1) in 76% yield.

2. Reaction of Diethyl Ethylenephosphoramidate with Diethylamine. A mixture of 5.3 g of diethyl ethylenephosphoramidate, 21.5 g of diethylamine, and about 0.1 g of ammonium chloride was heated in a sealed tube at 80-85° for 28.5 hours. The excess of amine was distilled off under reduced pressure. Two fractiona-

TABLE 2

Dialkyl 2-Chloroethylphosphoroamidates

No.	Formula of substance	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated	Phosphorus content (%) found	Phosphorus content (%) calculated	Yield (%)
1	$(CH_3O)_2PNH-CH_2-CH_2Cl$ ‖ O	114—115 (1.5)	1.2900	1.4537	39.16	39.74	16.71; 16.87	16.58	79.5
2	$(C_6H_5O)_2PNH-CH_2-CH_2Cl$ ‖ O	148 (5)	1.1865	1.4473	48.57	48.97	14.31	14.39	65
3	$(n\text{-}C_3H_7O)_2PNH-CH_2-CH_2Cl$ ‖ O	123—124 (0.7)	1.1297	1.4478	57.68	58.21	12.76; 12.86	12.74	72.5
4	$(i\text{-}C_3H_7O)_2PNH-CH_2-CH_2Cl$ ‖ O	104—106 (1.0)	1.1090	1.4404	57.91	58.21	12.95; 13.06	12.74	73
5	$(n\text{-}C_4H_9O)_2PNH-CH_2-CH_2Cl$ ‖ O	148.5—150 (1.7)	1.0847	1.4490	67.25	67.45	11.60; 11.71	11.42	74.5
6	$(i\text{-}C_4H_9O)_2PNH-CH_2-CH_2Cl$ ‖ O	136.5—138 (1.7)	1.0761	1.4458	67.25	67.45	11.71; 11.48	11.42	62
7	$(i\text{-}C_5H_{11}O)_2PNH-CH_2-CH_2Cl$ ‖ O	153—153.5 (1.4)	1.0552	1.4495	76.21	76.68	10.56, 10.45	10.36	60.5

tions of the residue gave 4.5 g (65.7%) of a liquid, b.p. 104-105° (1 mm); d_4^{20} 1.0157; n_D^{20} 1.4439; Found MR 65.97; Calculated MR 66.52

Found %: P 12.70; 12.62
$C_{12}H_{27}N_2O_3P$. Calculated %: P 12.30

3. Addition of Ethyl Bromide to Diethyl 2-Diethylaminoethylphosphoramidate (I). A mixture of 1.6 g of the substance (I) with a large excess of ethyl bromide (3 ml) was allowed to stand at room temperature; after several hours crystals began to form. After five days the excess of ethyl bromide was removed, and 2.25 g of crude crystals were obtained (98% yield). After recrystallization from ethyl bromide the substance melted at 135-137° (the crystals became wet before melting); a further recrystallization did not effect the melting point.

Found %: P 8.42; 8.77
$C_{13}H_{30}BrN_2O_3P$. Calculated %: P 8.59

4. Reaction of Diethyl Ethylenephosphoramidate (I) with Benzenethiol. A solution of 10 g of the substance (I) and 6.15 g of benzenethiol in 50 ml of carbon tetrachloride was stirred at room temperature for seven hours, after which the mixture was set aside overnight. On the next day the contents of the flask were heated to 50° and stirred at this temperature for one hour. When the solvent was distilled off, the starting substances were obtained together with a small amount of a substance of b.p. 105-115° (4 mm). The substances were mixed together again and heated under reflux at 80-85° for seven hours. Two fractionations from an Arbuzov flask gave a fraction of b.p. 195-198° (2 mm); n_4^{20} 1.5288; d_D^{20} 1.1655; Found MR 76.45; Calculated MR 76.43. The yield was 62%.

Found %: P 10.74; 10.79
$C_{12}H_{28}NO_3PS$. Calculated %: P 10.73

5. Synthesis of Dialkyl 2-Chloroethylphosphoramidates. The conditions of the synthesis were not changed. A solution of 6.6 g (0.153 mole) of ethylenimine in 25 ml of chloroform was dropped into a solution of 30.7 g (0.153 mole) of dipropyl phosphorochloridate in 75 ml of chloroform (which was cooled to −15°) for 50 minutes with stirring. The mixture was maintained at a temperature of from −15° to 0° for one hour, after which the cooling bath was removed and the mixture was set aside at room temperature overnight. Chloroform was distilled off under reduced pressure. Two distillations from an Arbuzov flask gave fairly pure Substance 3 (Table 2) in 72.5% yield.

SUMMARY

1. By the action of ethylenimine on dialkyl phosphorochloridates in presence of triethylamine, the corresponding dialkyl ethylenephosphoroamidates were prepared in high yield.

2. A study was made of the products obtained by reaction of diethyl ethylenephosphoramidate with diethylamine and with benzenethiol.

3. It was shown that the reactivity of the ethylenimine ring is lowered by replacement of the imine hydrogen by the dialkoxyphosphinyl group.

4. By the action of ethylenimine on dialkyl phosphorochloridates in absence of a base, the corresponding dialkyl 2-chloroethylphosphoramidates were prepared.

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ACTION OF ACTIVE NITROGEN ON ORGANIC SUBSTANCES.

COMMUNICATION 1

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Among the numerous investigations devoted to the study of the nature of active nitrogen and its afterglow, only a few are concerned with the action of active nitrogen on organic substances. In 1911 Strutt [1] showed by means of qualitative experiments that active nitrogen reacts with organic substances with formation of hydrogen cyanide and, in some cases, a dark-colored resinous substance that formed on the walls of the vessel. Also, in the reaction with benzene the odors of benzonitrile and phenyl isocyanide were detected. Much later, in 1938 [2], diphenylacetylene, benzonitrile, tetrahydronaphthalene, and isoprene were submitted to the action of active nitrogen. The authors again observed the formation of hydrogen cyanide, which was determined quantitatively, and a macromolecular deposit, which contained 16-28% of nitrogen. In the course of the last five years there has appeared a series of papers by Winkler and coworkers, who made a detailed investigation of the reactions of active nitrogen with various aliphatic hydrocarbons, namely, methane and ethane [3], propane [4], butane and isobutane [5], ethylene [6], propene [7], isobutene [8], and acetylene [9]. The rates of formation of the reaction products were determined.

It will be seen that, as yet, the reactions of active nitrogen with organic substances have been studied for only a very limited number of cases. We considered it to be of interest to extend the range of these compounds to some extent with the object of comparing the reactivities of organic substances of various classes toward active nitrogen. As a criterion in the appraisal of the reactivities of the substances we took the amount of nitrogen that reacted. A study was made of the action of active nitrogen on certain hydrocarbons, carbonyl compounds, carboxylic acids, and esters. In these reactions the formation of hydrogen cyanide was observed, and in some cases there was also a dark-colored deposit, which formed on the walls of the reaction vessel. Also, some reaction products condensed, together with the original substance, in traps cooled with liquid nitrogen.

Stearic and oleic acids and oleic and phthalic esters were treated in the liquid state with active nitrogen. Under these conditions only a very small amount of hydrogen cyanide was obtained (a few milligrams per hour). On the other hand, the reaction of active nitrogen with acetic acid in the form of vapor was considerably more vigorous: the amount of hydrogen cyanide formed was almost ten times as great as in the reaction with liquid stearic acid, even though the latter experiment was carried out at a high temperature. This increase in the amount of hydrogen cyanide formed cannot be attributed to the difference in reactivity between acetic and stearic acids, but is clearly determined by the difference in state of aggregation: when atomic nitrogen passes through a liquid, its concentration must fall sharply owing to recombination.

In experiments with vapors a cylindrical tube was used at first, but later the tube was replaced by a [illegible] sphere. It was found that in the sphere, i.e. with reduction in the degree of deactivation of nitrogen on the walls of the vessel, the amount of hydrogen cyanide formed was increased to several times the amount formed in the tube. These results show that the formation of hydrogen cyanide occurs in the gas space. It must be pointed out the relatively large amount of hydrogen cyanide formed is accompanied by only traces of cyanogen.

The deposit is formed exclusively on the walls of the reaction vessel. In appearance and properties the deposit is similar to the polymerization product of hydrogen cyanide, and also to the cyanogen polymer obtained by Syrkina and Shekhter [10] by passing a discharge through cyanogen. If the deposit that we obtained were also a polymerization product of HCN or CN, then its formation should have been observed in the reactions of active nitrogen with all organic substances. It was actually found that the deposit was formed only in

reactions with unsaturated and aromatic compounds. The only exception was cyclohexanone, which, however, formed considerably less deposit than benzaldehyde, benzene, naphthalene, and cyclohexene. It is evident that, in the formation of the deposit, radicals or molecules other than HCN and CN take part, and this is confirmed also by the atomic ratio of carbon to nitrogen. For example, in the solid reaction product from benzene C : N is approximately 2, and in the product from cyclohexene there are almost four carbon atoms to each nitrogen atom. Apart from C, H, and N, the deposits contain silicon (the presence of which is probably to be explained by the formation of silicon nitrides in the discharge tube) and oxygen, traces of which are present in the nitrogen entering the system. When the deposits were hydrolyzed with 30% caustic potash solution, 82-84% of the nitrogen contained in the deposits was eliminated as ammonia. The comparatively ready elimination of ammonia indicates that the deposits probably contain imine or nitrile groups. Versteeg and Winkler [9], who base their views on other considerations, also believe that the deposit obtained in the reaction between acetylene and active nitrogen contains nitrile groups.

The identification of the reaction products condensed in the cooled traps would undoubtedly be of interest, but the investigation of these products is greatly complicated by the fact that they are formed in extremely small amount. Moreover, in certain cases and particularly in the reaction with benzaldehyde, the mixture of products is so complex that we have been unable to isolate pure substances. We succeeded in isolating and identifying some of the reaction products that collected in the traps only in the experiments with benzene, naphthalene (see Communication 2), and cyclohexanone.

In the reaction with cyclohexanone we isolated relatively large amounts of its cyanohydrin, which was formed by the addition of HCN to unchanged ketone. It would be expected that in the reaction between active nitrogen and benzaldehyde the corresponding cyanohydrin would again be formed, but we were unable to isolate any. Boiling of the mixture of products with hydrochloric acid yielded a little of a substance that was probably mandelic acid.

The liquids that were treated with active nitrogen became darker in color, became more viscous, and absorbed nitrogen to the extent of several percent. From the product obtained by treating oleic acid with active nitrogen, a little stearic acid was isolated. It is evident that the action of active nitrogen resulted in the elimination of hydrogen, which then hydrogenated the oleic acid. A similar phenomenon was observed previously [11] when oleic acid was subjected to a glow discharge in an atmosphere of air or nitrogen. This observation is also in accord with the results of Winkler and coworkers [6-8] on the formation of saturated hydrocarbons during the treatment of ethylenic hydrocarbons with active nitrogen.

The results of all the experiments carried out are given in the Table, but in an examination of these results it should be borne in mind that it is difficult to compare the experiments on liquids with the remaining experiments, in which the substances reacted in the vapor state. Moreover, the duration of the first experiments was only 10-15 hours, whereas we later increased the duration to 40-50 hours because we considered that the average values so obtained would represent the actual values more accurately.

For the experiments on liquids, a comparison based on the amount of hydrogen cyanide formed indicates that the presence of a double bond in the molecule of a carboxylic acid greatly raises its reactivity toward active nitrogen (compare the results on oleic and stearic acids) and that esters of aromatic carboxylic acids are more stable to active nitrogen than esters of unsaturated aliphatic acids. The data on the reaction with benzaldehyde cannot be regarded as complete, for products that condensed in the traps in fairly large amounts were not investigated.

A comparison of the total amounts of nitrogen reacting (Column 14 in the table) shows that cyclohexene reacts most readily with active nitrogen; then follows hexane and cyclohexane; and of the hydrocarbons investigated, benzene is the most stable to the action of active nitrogen (the experiments with naphthalene were inconclusive, owing to the inadequate amount of its vapor present in the reactor). The higher reactivity of hexane, as compared with cyclohexane, indicates that cyclization confers stability on the substance.

EXPERIMENTAL

Nitrogen was passed from a cylinder, through a drying system, over heated copper turnings, and finally to the discharge tube. The working p.d. of the tube was 2100-2500 v and the average current was 140-180 ma;

TABLE

No.	Substance		Form of reaction	Duration of reaction (hours)	Amount of ingoing nitrogen (g)	Products formed				Amount of nitrogen that reacted					Notes
	Name	State of aggregation				HCN (mg/hour)	Deposit			with formation of			altogether		
							(mg/hour)	N content (%)	C content (%)	HCN (mg/hour)	deposit (mg/hour)	other products (mg/hour)	(mg/hour)	(% on ingoing nitrogen)	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Stearic acid	Liquid	Test tube	15	210	1.6	Nil	Nil	Nil	–	–	–	–	–	Temperature of stearic acid 70°
2	Oleic acid	"	" "	10	140	7.7	"	"	"	–	–	–	–	–	Temperature of oleic acid 70°
3	Ditto	"	" "	15	210	1.7	"	"	"	0.9	–	1.2	2.1	0.15	After reaction substance contains 3.3% N
4	Dibutyl phthalate	"	" "	15	210	3.1	"	"	"	1.6	–	2.4	4.0	0.03	After reaction substance contains 2.3% N
5	Butyl oleate	"	" "	15	210	4.2	"	"	"	–	–	–	–	–	
6	Acetic acid	Vapor	Tube	10	140	15.6	"	"	"		–	–	8.1	0.06	
7	Hexane	"	"	15	435	53.6	"	"	"	27.8	–	–	27.8	0.095	
8	"	"	Sphere	50	1450	117.6	"	"	"	60.6	–	–	60.6	0.21	
9	Cyclohexane	"	Tube	50	1450	31.0	"	"	"	16.1	–	–	16.1	0.05	
10	"	"	Sphere	15	435	91.9	"	"	"	47.6	–	–	47.6	0.16	
11	Cyclohexene	"	"	50	1450	140.5	15.8	16.7	59.2	72.8	2.6	–	75.4	0.26	
12	Benzene	"	Tube	50	700	10.2	15.6	25.2	49.7	5.3	3.9	–	9.2	0.06	
13	"	"	Sphere	50	1450	45.3	Not determined			23.5	–	–	–	–	
14	Naphthalene	"	"	50	700	6.4	22.8	18.9	50.3	3.3	4.3	–	7.6	0.05	
15	Cyclohexanone	"	"	44	1275	23.6	7.5	15.0	52.47	12.2	1.1	4.5	17.8	0.06	The cyanohydrin was obtained at 25.2 mg/hour and a substance containing 12.6% N was obtained at 13 mg/hour
16	Benzaldehyde	"	"	38	1100	18.8	74.0	15.5	54.6	9.7	11.5	–	–	–	

the pressure was 10-15 mm. In reactions with liquids, the glowing glass, after leaving the discharge tube, was bubbled through the substance, which was contained in a test tube placed at a distance of 18 cm from the anode of the discharge tube.

In reactions with gaseous substances, the reaction vessel was either a tube (diameter 2.5 cm) or a sphere (diameter 12 cm). The vapor of the substance passed into the reaction vessel at a distance of 18 cm from the discharge through the capillary end of a glass tube sealed into the reaction vessel and provided with a tap. In the reaction with naphthalene, the substance was poured into the sphere so as to form a thin layer. In the experiments on cyclohexane and benzaldehyde the substances were again evaporated directly in the sphere, into which they were introduced in the form of small drops.

In the course of a single day, the reaction was continued for 5-7 hours. The discharge was then switched off, and the volatile reaction products were driven from the traps into an absorption vessel containing 5% caustic potash solution; the resulting solution was titrated with 0.1 N silver nitrate by Liebig's method. If a deposit formed on the walls during the reaction, then at the end of the whole experiment the reaction sphere or tube was filled with methanol and set aside for two days, after which the undissolved part of the deposit was readily scraped off. Some heat was evolved when active nitrogen reacted with the various substances, and the reaction was carried out at 25-30°.

Experiments with Oleic Acid. After the reaction the test tube contained a brown viscous oil having a green fluorescence; it was treated with ether. The ether solution was shaken with dilute caustic soda solution, and acidification of the aqueous layer yielded a light-yellow precipitate (35 mg), which melted at 63-64° after crystallization from methanol; in admixture with stearic acid it melted at 64-65°.

Experiments with Cyclohexene. In order to determine cyanogen, after an eight-hour reaction the volatile products were distilled into absorption vessels containing silver nitrate solution. The gases leaving these vessels were passed into absorption vessels containing caustic potash solution. The amount of cyanogen found was 6.78 mg, i.e. 0.84 mg/hour. A weighed amount (0.2556 g) of the deposit on the walls was dissolved in 10 ml of 30% caustic potash solution, and the solution was boiled for 25 hours, the liquid that distilled over being collected in 50 ml of 0.1 N HCl. Constant volume of the solution heated was maintained by addition of water. Found 0.03514 g N (82.1% on the amount taken).

Experiments with Benzene. In order to determine cyanogen, after an eight-hour reaction the volatile products were absorbed in 5% aqueous ammonia. One half of the solution from the absorption vessels was evaporated down: the dry residue weighed 3.6 mg, which corresponds, when calculated for the whole volume, to 5.6 mg of cyanogen, i.e. 0.7 mg/hour. The other half of the solution was titrated with silver nitrate solution, and the result corresponded to 364 mg. of hydrogen cyanide in the whole volume. The alcohol-insoluble deposit contained 48.78% C, 5.59% H, 26.41% N, and 5.3% of ash; 0.1516 g of it was boiled for 20 hours with 10 ml of 30% caustic potash solution. Found 0.0335 g N (84% on the amount taken).

Sulfuric acid was added to the alkaline solution remaining in the flask until the mixture was acid in reaction. The voluminous precipitate that formed was soluble in concentrated caustic potash solution. It did not burn or char, and it did not give a qualitative reaction for molybdenum *. It was soluble in a mixture of sulfuric and hydrofluoric acids, and the resulting solution evaporated away completely when heated.

Experiments with Naphthalene. When the alcohol-insoluble deposit (0.1336 g) was hydrolyzed, 0.0213 g N (84.4% on the amount taken) was distilled off as ammonia. In order to prove the presence of ammonium chloride in the solution, 400 ml was evaporated to dryness; weight of residue 0.71 g. Crystallization from water gave a white crystalline substance, which sublimed readily above 300°.

Experiments with Cyclohexanone. Hydrogen cyanide was distilled from the contents of the cooled traps, which were then washed out with cyclohexanone. The resulting solution was vacuum-distilled. A colorless oil (1.11 g) was collected at 97° (3 mm).

* It is possibly meant that it did not give a molybdate reaction (for silica). — Translator.

Found %: C 67.31; H 8.04; N 10.94

$C_7H_{11}ON$. Calculated %: C 67.16; H 8.86; N 11.19

The residue from the distillation was a dark-brown viscous liquid containing 12.58% N.

A mixture of 0.5 g of the cyclohexanone cyanohydrin so obtained and 1.5 ml of concentrated hydrochloric acid was boiled for three hours. The cooled reaction mixture was extracted with ether. The residue remaining after removal of ether was dissolved in sodium carbonate solution, and the solution was washed with ether and acidified. Crystallization from a benzene-hexane mixture gave 0.16 g of 1-hydroxycyclohexanecarboxylic acid, m.p. 105-106° (the literature [12] gives 106-107°).

Found %: C 57.82; H 8.38

$C_7H_{12}O_3$. Calculated %: C 58.30; H 8.32

A mixture of 0.15 g of the cyclohexanone cyanohydrin, 0.15 g of cyclohexanone, and 1 ml of concentrated hydrochloric acid was allowed to stand for two days at room temperature. The precipitate of white crystals was filtered off and dried (0.14 g, m.p. 193-195°); after crystallization from alcohol it melted at 193.5-194.5° (Ultee [13] gives m.p. 194° for 1-(1-hydroxycyclohexyloxy) cyclohexanecarbonitrile).

Found %: C 69.72; H 9.52; N 6.15

$C_{13}H_{21}O_2N$. Calculated %: C 69.92; H 9.48; N 6.27

Experiments with Benzaldehyde. The contents of the traps were washed out with benzene, and the resinous residue was filtered off. The solution was washed with sodium carbonate solution, and benzene was distilled off down to a volume of about 10 ml. Concentrated hydrochloric acid (3 ml) was added to the residue, and the mixture was boiled for three hours. The benzene layer was treated with sodium carbonate solution, and this solution was then acidified and extracted with ether. Ether was removed, and crystallization of the residue from benzene gave white crystals, m.p. 107-111°; a mixture of this substance with benzoic acid melted at 83-88°.

SUMMARY

1. Comparison of the reactivities of some organic compounds toward active nitrogen showed that these compounds can be placed in the following series of diminishing reactivity: cyclohexene > hexane > cyclohexane > benzene > cyclohexanone > acetic acid > butyl oleate > dibutyl phthalate > oleic acid > stearic acid.

2. The main product in the reactions of active nitrogen with the organic compounds investigated was found to be hydrogen cyanide, the formation of which occurred in the general reaction space. Only traces of cyanogen were formed.

3. When unsaturated and aromatic compounds were treated with active nitrogen, solid substances containing 16-20% of nitrogen were formed on the walls of the vessel. In the alkaline hydrolysis of these substances, almost the whole of their nitrogen is eliminated as ammonia.

4. When cyclohexanone was treated with active nitrogen, a small deposit of cyclohexanone cyanohydrin was formed in addition to hydrogen cyanide.

5. Reaction between active nitrogen and oleic acid resulted in the formation of stearic acid.

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DEHYDROCHLORINATION OF TRICHLORO(CHLOROALKYL)- AND TRICHLORO(DICHLOROALKYL)-SILANES. REARRANGEMENT OF 1,1,1,2,4,4,4-HEPTACHLORO-1,4-DISILABUTANE DURING DEHYDROCHLORINATION WITH ALUMINUM CHLORIDE

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One method of synthesizing unsaturated organosilicon compounds consists in the elimination of HX from various halogen-containing organosilicon compounds. Ushakov and Itenberg [1], using this method, were the first to prepare the unsaturated silahydrocarbon $(C_2H_5)_3SiCH=CH_2$, HCl being eliminated with aid of alcoholic alkali from $(C_2H_5)_2SiClCH_2Cl$. This method was later modified by the replacement of alcoholic alkali by quinoline [2] or aluminum chloride [3]. These latter reagents enabled the scope of the method to be widened, for they can be applied to the dehydrochlorination of compounds in which both chloroalkyl groups and chlorine atoms are attached to silicon. However, the possibility of the extensive application of these reagents, particularly aluminum chloride, for dehydrochlorination has received extremely inadequate study. Moreover, there are no comparative data on their application. Only for one compound ($Cl_3SiCH_2CH_2Cl$) has dehydrochlorination been carried out both with quinoline [4] and with aluminum chloride [3].

Apart from the example cited above, aluminum chloride has been successfully applied to the dehydrochlorination of only three compounds: 1-, 2-, and 3-chloropropyltrichlorosilanes [5].

It is known also that, under the action of aluminum chloride, some 1-, 2-, and 3-chloroalkylsilanes undergo intramolecular rearrangement or decomposition instead of elimination of HCl [4, 6, 7]. The present investigation was undertaken with the object of determining the limits of the applicability of aluminum chloride and quinoline and of obtaining comparative material on the dehydrochlorination of the same compounds by both reagents.

TABLE 1

No.	Reagent		$AlCl_3$				Quinoline [8]		
	Original substance	Position of Cl	Product	Position of Cl	Yield (%) at 500 mm	Yield (%) at 100 mm	Product	Position of Cl	Yield (%)
1	$Cl_3SiCCl_2CH_3$	1,1	$Cl_3SiCCl=CH_2$	1	78	67	$Cl_3SiCCl=CH_2$	1	58
2	$Cl_3SiCH(CH_3)CH_2Cl$	1,2	$Cl_3SiCH=CHCl$	2	0	47	$Cl_3SiCCl=CH_2$	2	30.5
3	$Cl_3SiCH_2CHCl_2$	2,2	$Cl_3SiCH=CHCl$	2	78	52	$Cl_3SiCH=CHCl$	2	50

We distilled 1,1-, 1,2-, and 2,2-dichloroethyltrichlorosilanes in presence of aluminum chloride (the dehydrochlorination of these compounds with quinoline has been carried out recently by Sommer and coworkers [8]). The results obtained are shown in Table 1.

It is important to note that the yields of 1- and 2-chlorovinyltrichlorosilanes (No. 1 and 3) are 60% higher in presence of aluminum chloride than in presence of quinoline, and it is particularly notable that the two reagents give different results in the dehydrochlorination of trichloro (1, 2-dichloroethyl) silane (No. 2)*.

The dehydrochlorination of compounds No. 1 and 2 was effected by distilling them under reduced pressure in presence of catalytic amounts of aluminum chloride from a flask fitted with a fractionating column. When these experiments were carried out at atmospheric pressure, the yields of trichloro (chlorovinyl) silanes were reduced and the amount of silicon tetrachloride formed was increased. However, in the case of trichloro (1,2-dichloroethyl) silane, dehydrochlorination occurred only when the distillation was at atmospheric pressure.

Bailey and Pines [5] showed that the three trichloro (chloropropyl)silanes give high yields of mixture of allyl- and propenyl-trichlorosilanes when dehydrochlorinated with aluminum chloride. We attempted the dehydrochlorination with quinoline both of 2- and 3-chloropropyltrichlorosilanes and also of trichloro(2-chloro-2-methylpropyl) – and trichloro (3-chloro-2-methylpropyl)-silanes, which we have synthesized for the first time. It was found that the 2-chloro isomers gave, respectively, trichloropropenylsilane (61%) and trichloro (2-methylpropenyl) silane (70%), but HCl was not eliminated from the 3-chloro isomers.

Attempts to dehydrochlorinate dichloro(3-chloropropyl) methylsilane and (1-chloroethyl) triethylsilane by means of quinoline were also unsuccessful: after refluxing $(C_2H_5)_2SiCHClCH_3$ with quinoline for ten hours, only about 10% of $(C_2H_5)_2SiCH=CH_2$ was obtained. Agre [9] finds that $Cl_2SiCHClCH_3$, treated with quinoline, gives $Cl_2SiCH=CH_2$ in only 13% yield. The dehydrochlorination of trichloro(3-chloro-2-methylpropyl) silane with aluminum chloride resulted in the formation of a 1 : 1 mixture of 2-methylallyl- and 2-methylpropenyl-trichlorosilanes:

$$Cl_3SiCH_2\underset{CH_3}{C}HCH_2Cl \xrightarrow{AlCl_3} Cl_3SiCH_2\underset{CH_3}{C}=CH_2 + Cl_3SiCH=\underset{CH_3}{C}-CH_3.$$

When dichloro(3-chloropropyl) methylsilane was treated with aluminum chloride, it was decomposed almost quantitatively to CH_3SiCl_3. Comparative results on dehydrochlorination with quinoline and with aluminum chloride are given in Table 2.

Hence, it will be seen from our results and the data in the literature that quinoline is mainly suitable for the dehydrochlorination of chloro(2-chloroalkyl) silanes, which it converts exclusively into compounds having the double bond in the 1-position. On the other hand, aluminum chloride, which eliminates HCl not only from 2-chloroalkyl-, but also from 1- and 3-chloroalkyl-trichlorosilanes, gives a mixture of compounds in which the double bond is in the 1- and 2-positions. However, even if only one of the three chlorines attached to silicon in 1-, 2-, and 3-choloroalkyltrichlorosilanes is replaced by an alkyl radical, the use of aluminum chloride is already impossible: elimination of HCl does not occur, but the 1-chloroalkyl compounds may undergo rearrangement or decomposition [6] and the 2- and 3-chloroalkyl compounds may undergo so-called β- and γ-breakdown [4, 7].

Interesting results were obtained in the dehydrochlorination – both with quinoline and with aluminum chloride – of 1,1,1,2,4,4,4-heptachloro-1,4-disilabutane (V). When quinoline was used, a 70% yield was obtained of 1,2-bistrichlorosilylethylene [1,1,1,4,4,4-hexachloro-1,4-disilabut-2-ene] (XIII), m.p. 36.1°, which was then methylated to 1,2-bistrimethylsilylethylene [2,2,5,5-tetramethyl-2,5-disilahex-3-ene] (XIV) (see scheme of reactions below). However, the physical properties of (XIV), as compared with those of its structural analogs containing single and triple bonds, and particularly its high exaltation of molecular refraction (+ 0.83) (Table 3) at first caused us to doubt the purity of the product, in spite of the satisfactory analytical data.

* Pyrolysis of this compound at 610° gives a mixture of 1- and 2-chlorovinyltrichlorosilanes in 43% yield [9].

The synthesis of this compound was therefore carried out by another method: the condensation of $(CH_3)_2SiCH=CHCl$ with $(CH_3)_3SiCl$ in presence of sodium.

TABLE 2

No.	Original compound	Reagent: Quinoline — Product	Quinoline — Yield (%)	Reagent: $AlCl_3$ — Product	$AlCl_3$ — Yield (%)
1	$Cl_2SiCH_2CHClCH_3$	$Cl_2SiCH=CHCH_3$	61	$Cl_2SiCH=CHCH_3$ / $Cl_2SiCH_2CH=CH_2$ } 2 : 1[5]	53.5
2	$Cl_2SiCH_2CH_2CH_2Cl$	Original compound	—	$Cl_2SiCH=CHCH_3$ / $Cl_2SiCH_2CH=CH_2$ } 3 : 1[5]	68
3	$Cl_2SiCH_2C(CH_3)_2$ (Cl)	$Cl_2SiCH=C(CH_3)_2$ (CH$_3$)	76.5	—	—
4	$Cl_2SiCH_2CHCH_2Cl$ (CH_3)	Original compound	—	$Cl_2SiCH=C(CH_3)_2$ / $Cl_2SiCH_2C=CH_2$ (CH_3) } 1 : 1	47
5	$CH_3Cl_2SiCH_2CH_2CH_2Cl$	Original compound	—	CH_3SiCl_3	85
7	$(C_2H_5)_2SiCHClCH_3$	$(C_2H_5)_2SiCH=CH_2$	10		

By an analogous method we synthesized the isomer of (XIV), 1,1-bistrimethylsilylethylene [2,2,4,4-tetramethyl-3-methylene-2,4-disilapentane] (XV). (2-Chlorovinyl) trimethylsilane was prepared by the methylation of $Cl_2SiCH=CHCl$.

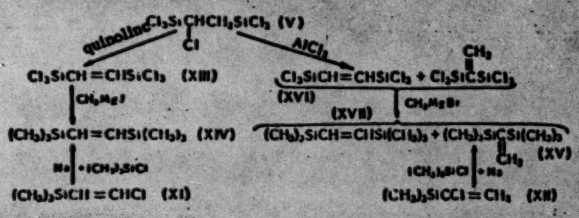
It should be noted that, on analogy with $Cl_2SiCH_2CH_2Cl$, which is decomposed by CH_3MgBr with formation of ethylene and $(CH_3)_4Si$[12], it might be expected that the methylation of $Cl_2SiCH=CHCl$ would not go. However, both the methylation of $Cl_2SiCH=CHCl$ and the Wurtz reaction of the resulting $(CH_3)_2SiCH=CHCl$ with $(CH_3)_3SiCl$ went without any decomposition of the molecule - a difference in behavior not only from $Cl_2SiCH_2CH_2Cl$, but also from compounds of the type M–CH=CHCl [13] (M may be Pb, Sn, and other metals), which are decomposed with elimination of ethylene and acetylene respectively under the action of various reagents, including RMgX.

TABLE 3

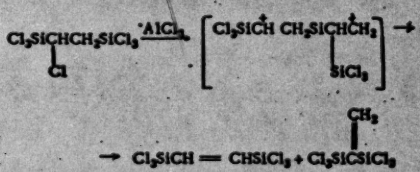
Formula of substance	B.p. (°C)	n_D^{20}	d_4^{20}	MR found	MR calculated	Δ
$(CH_3)_2SiCH_2CH_2Si(CH_3)_2$ [10]	150—151	1.4204	0.7536	58.00	58.43	+0.17
$(CH_3)_2SiCH=CHSi(CH_3)_2$	145	1.4310	0.7589	58.79	57.96	+0.83
$(CH_3)_2SiC\equiv CSi(CH_3)_2$ [11]	134	1.4200	0.7703	58.65	56.82	−0.17

Comparison of the properties of the isomers (XIV) and (XV) showed that they are greatly different. The compound (XIV) shows a high exaltation of MR, whereas (XV) shows practically none. Moreover, whereas the characteristic Raman lines for (XIV) are fairly intense and have breadths of up to 20 cm^{-1}, these lines can scarcely be observed in the spectrum of (XV). The rate of addition of thiocyanogen to (XIV) was found to be ten times as high as that for (XV). Finally, whereas no polymer could be obtained from (XIV) in presence of a peroxide, even at a pressure of 5500 atm, (XV) gave a pentamer under these conditions.

When (V) was distilled with aluminum chloride, the dehydrochlorination product was a liquid (m.p. from −10 to + 10°). This was methylated, and the Raman and infrared spectra of the product were investigated (by Yu. P. Egorov); it was thus shown that the product was a mixture of (XIV) and (XV).



The hypothesis that (XIII) could isomerize into (XVI) under the influence of aluminum chloride was not confirmed, for distillation of (XIII) with aluminum chloride, even at atmospheric pressure (~195°), did not affect its melting point, and subsequent methylation of the product gave only (XIV). We must conclude, therefore, that the dehydrochlorination of 1,1,1,2,4,4,4-heptachloro-1,4-disilabutane with aluminum chloride is accompanied by partial isomerization of the 1,2-substituted carbonium ion into the more stable 2,2-substituted carbonium ion [3, 5]:



EXPERIMENTAL

Trichloroisobutylsilane $CH_3CHCH_2SiCl_3$ (I)

A solution of isobutylmagnesium bromide, prepared in 1.3 liters of ether from 85 g of magnesium and 530 g of isobutyl bromide, was added with stirring and cooling to a mixture of 665 g of silicon tetrachloride and 500 ml of ether contained in a three-liter flask. On the next day the contents of the flask were boiled for five hours and then filtered from the precipitate of magnesium salt. Ether was distilled from the filtrate, and the residue was distilled through a column. The product, which came over at 140-142°, was 359 g of the substance (I); yield 54%; b.p. 140.6° (746); n_D^{20} 1.4349; d_4^{20} 1.1590; Found MR 43.11; Calculated MR 43.06.

Trichloro(1-chloro-2-methylpropyl)silane $CH_3CHCHSiCl_3$ (II)
CH_2Cl

Trichloro(2-chloro-2-methylpropyl)silane $CH_3C(Cl)CH_2SiCl_3$ (III)
CH_3

Trichloro(3-chloro-2-methylpropyl)silane $CH_2CHCH_2SiCl_3$ (IV)
CH_2Cl

Substance (I) (356 g) was placed in the flask of the apparatus [14]. Chlorination was continued until the temperature in the flask reached 174° (28 hours). Three distillations through a column gave four fractions: Fraction I, b.p. 140-143°, was 109 g of unchanged (I); Fraction II, b.p. 161-164°, 27 g, n_D^{20} 1.4668; d_4^{20} 1.2665, was the 1-chloro compound (II), apparently mixed with dehydrochlorination products (found MR 49.50, calculated MR 47.90); Fraction III, b.p. 179-181°, 34 g, was the 2-chloro compound (III), b.p. 179.5° (740 mm), n_D^{20} 1.4660; d_4^{20} 1.3110; Found MR 47.74; Calculated MR 47.90; Fraction IV, b.p. 191-192°, 138 g, was the 3-chloro isomer (IV), b.p. 192.0° (740 mm), n_D^{20} 1.4680; d_4^{20} 1.3114, Found MR 47.92; Calculated MR 47.90; the yield of monochlorinated products was 77%.

The chlorinations referred to below were carried out similarly.

1,1,1,2,4,4,4-Heptachloro-1,4-disilabutane $Cl_3SiCHCH_2SiCl_3$ (V)
Cl

The chlorination of 343 g of 1,1,1,4,4,4-hexachloro-1,4-disilabutane was continued for 26 hours, in the course of which the temperature in the flask rose to 221°. Distillation through a column gave 123 g of the original substance, b.p. 200-202°, and 230 g of (V), b.p. 224-225°. The yield of (V) on the amount of hexachloro-disilabutane that reacted was 94%. M.p. −40 ± 5°; b.p. 225.0° (737 mm); n_4^{20} 1.4915; d_4^{20} 1.5774; Found MR 60.89; Calculated MR 61.05.

Trichloro(1,1-dichloroethyl)silane $CH_3Cl_2CSiCl_3$ (VI)

Trichloro(1,2-dichloroethyl)silane $ClCH_2ClCHSiCl_3$ (VII)

Trichloro(2,2-dichloroethyl)silane $Cl_2CHCH_2SiCl_3$ (VIII)

A. Trichloro(1-chloroethyl)silane [15] (482 g) was chlorinated for 18 hours, in the course of which the temperature in the flask rose to 151°. Distillation gave 225 g of the original 1-chloroethyl compound, b.p. 136.8° and n_D^{20} 1.4646, 167 g of (VI), b.p. 151.8°, and 100.5 g of (VII), b.p. 181° (760 mm); n_D^{20} The yield of (VI) and (VII) was 88.5%, the relative amounts of the isomers being 1 : 0.6.

B. Trichloro(2-chloroethyl)silane [15] (1265 g) was chlorinated for 53 hours, in the course of which the temperature in the flask rose to 174°. Distillation gave 269 g of the original 2-chloroethyl compound and 1080 g of a difficultly separable mixture of (VII) and (VIII), b.p. 170-180°, yield 92.5%. Pure (VIII) was obtained with the aid of sulfuryl chloride [8]; b.p. 175° (740 mm); n_D^{20} 1.4800; d_4^{20} 1.5201; Found MR 43.43; Calculated MR 43.48.

Trichloro(1-chlorovinyl)silane $CH_2{=}ClCSiCl_3$ (IX)

A. A mixture of 78 g of (VI) and 1 g of aluminum chloride was distilled at the usual rate at a pressure of 200-250 mm from a flask fitted with a column (300 mm in height, 20 mm in diameter) filled with porcelain rings 3-4 mm in diameter. Fractionation of the distillate through a column gave 2 ml of a fraction of b.p. 100-124°, 32 ml of a fraction of b.p. 124-127°, and 2.5 ml of a fraction of b.p. 127-140°. A yield of 51 g (77.9%) of (IX) was obtained; it had b.p. 124.6° (739 mm); n_D^{20} 1.4650; d_4^{20} 1.4243; Found MR 38.00; Calculated MR 38.17. The literature [8] gives b.p. 124°.

B. A mixture of 57 g of (VI) and 0.5 g of aluminum chloride was distilled at atmospheric pressure. The yield of (IX) was 32.2 g (67%). Subsequent experiments on dehydrochlorination with aluminum chloride were carried out under similar conditions.

Trichloro(2-chlorovinyl)silane ClCH=CHSiCl$_3$ (X)

A. A mixture of 97 g of (VIII) and 1 g of aluminum chloride was distilled at 300 mm. The yield of (X) was 64 g (78.2%); b.p. 133-136°.

B. Distillation of 57 g of (VIII) in presence of 0.5 g of aluminum chloride at atmospheric pressure gave 25g (52.1%) of (X), which came over at 133-135°. It had b.p. 133° (731 mm); n_D^{20} 1.4750; d_4^{20} 1.4364; Found MR 38.37; Calculated MR 38.17. The literature [8] gives b.p. 134°.

C. A mixture of 58 g of (VII) and 0.5 g of aluminum chloride was distilled at atomospheric pressure. The product was 23 g (47%) of (X), b.p. 133-135° and n_D^{20} 1.4751; yield 47%.

(2-Chlorovinyl)trimethylsilane ClCH=CHSi(CH$_3$)$_3$ (XI)

A solution of methylmagnesium iodide in 1 liter of ether was prepared from 43 g of magnesium and 300 g of methyl iodide, and it was stirred while 99 g of (X) was added over a period of one hour. The mixture was boiled for four hours, and on the next day the product was decomposed by addition of water. The ether layer, combined with ether extracts of the aqueous layer, was dried with calcium chloride. Distillation through a column gave 42 g (52%) of (XI), b.p. 116.6° (741 mm); n_D^{20} 1.4380; d_4^{20} 0.8921; Found MR 39.63; Calculated MR 39.28.

	Found %:	C 44.73; 44.6;	H 8.33; 8.30;	Cl 26.80; 26.70;	Si 20.63; 20.45
$C_5H_{11}ClSi$.	Calculated %:	C 44.59;	H 8.31;	Cl 26.33;	Si 20.83

(1-Chlorovinyl)trimethylsilane CH$_2$=ClCSi(CH$_3$)$_3$ [8] (XII)

To methylmagnesium iodide prepared in 1 liter of ether from 45 g of magnesium and 320 g of methyl iodide, 100 g of (IX) was added over a period of one hour. After a one-hour boil and the usual treatment, distillation through a column gave 42 g (61%) of (XII), b.p. 104°.

1,2-Bistrichlorosilylethylene [1,1,1,4,4,4-Hexachloro-1,4-disilabut-2-ene] Cl$_3$SiCH=CHSiCl$_3$ (XIII)

A mixture of 167 g of (V) and 85 g of quinoline was distilled from a 250-ml flask up to a temperature of 210°. Redistillation through a column gave 110 g (74%) of (XIII), b.p. 190.5° (740 mm), m.p. + 36.1°.

	Found %:	C 7.96; 8.26;	H 0.95; 0.85;	Si 19.13; 18.78
$C_2H_2Cl_6Si_2$.	Calculated %:	C 8.15;	H 0.68;	Si 19.03

Dehydrochlorination of (V) with N,N-diethylaniline gave a 58% yield of (XIII). The dissolution of 1,2-bistrichlorosilylethylene in ether is accompanied by considerable cooling. The substance slowly absorbs bromine.

1,2-Bistrimethylsilylethylene [2,2,5,5-Tetramethyl-2,5-disilahex-3-ene] (CH$_3$)$_3$SiCH=CHSi(CH$_3$)$_3$ (XIV)

A. Methylmagnesium iodide was prepared in 300 ml of ether from 24.3 g of magnesium and 170 g of methyl iodide, and to the resulting solution melted (XIII) (42 g) was added dropwise. The ether was distilled off, and the residue in the flask was heated in a boiling water bath for more than nine hours. The ether that had been distilled off was then returned to the flask, and the contents were decomposed with water and given the usual treatment. Distillation through a column gave 22 g (89.5%) of (XIV), b.p. 145.0° (760 mm); m.p. −18.5°; n_D^{20} 1.4310; d_4^{20} 0.7589; Found MR 58.79; Calculated MR 57.96.

	Found %:	C 56.06; 55.99;	H 11.82; 11.69;	Si 32.59; 32.35
$C_8H_{20}Si_2$.	Calculated %:	C 55.74;	H 11.69;	Si 32.55

Δ ν (cm^{-1}): 183 (2), 228 (1), 325 (2), 610 (20), 683 (1), 698 (3), 789 (0), 842 (0), 1248 (1), 1258 (1), 1295 (3), 1387 (0), 1412 (1), 1551–1570 (2), 2900 (10), 2982 (2), 2961 (10).

B. Sodium (10 g) was melted in 60 ml of boiling isooctane and converted into dust with the aid of a rapidly rotating stirrer. When the mixture was cool, addition was made of 250 ml of ether, 25 g of chlorotrimethylsilane, about 2 ml of (XI), and, after 10 minutes, 0.5 ml of ethyl acetate. After one minute reaction set in accompanied by steady boiling of the ether, and the reaction was maintained by addition of 27 g of (XI) over a period of two hours. The contents of the flask were boiled further for four hours, and on the next day they were filtered from salt, which was washed with fresh ether. The residue remaining after distillation of ether was fractionated through a column and gave 34 g (76%) of (X), b.p. 145.5° (750 mm); n_D^{20} 1.4308; d_4^{20} 0.7591; Found MR 58.76; Calculated MR 57.96. The Raman spectrum was completely identical with the spectrum of (XIV) obtained by method A.

1,1-Bistrimethylsilylethylene [2,2,4,4-tetramethyl-3-methylene-2,4-disilapentane] $[(CH_3)_3Si]_2C=CH_2$ (XV)*

Ether (500 ml), chlorotrimethylsilane (20 g), (XII) (1 ml), and ethyl acetate (about 1.5 ml) were added to 9 g of sodium granulated in 30 ml of toluene. When reaction had begun, 23.5 g of (XII) was added in such a way that the ether boiled steadily. After a 2.5 hour boil and the usual treatment, distillation through a column gave 14 g (46.5%) of (XV), b.p. 151.6° (757 mm); m.p. below −70°; n_D^{20} 1.4374; d_4^{20} 0.7823; Found MR 57.76; Calculated MR 57.96.

Found %: C 55.97; 55.99; H 11.50; 11.58; Si 32.55; 32.57
$C_8H_{20}Si_2$. Calculated %: C 55.74; H 11.69; Si 32.55

Δ ν (cm^{-1}): 229 (4), 419 (2), 472 (5), 586 (2), 646 (7), 694 (4), 1251 (3), 1401 (2), 1418 (2), 1422 (2), 2898 (10), 2969 (10), 3014 (3).

1,1- and 1,2-Bistrichlorosilylethylenes $Cl_3SiCH=CHSiCl_3$ and $Cl_3SiC(SiCl_3)=CH_2$ (XVI)

A. A mixture of 225 g of (V) and 5 g of aluminum chloride was distilled at 10 mm. Redistillation through a column gave about 4 g of material boiling over the range 70-170° and 164 g (82%) of the substance (XVI), b.p. 190-195°; f.p. −8 to +9°; n_D^{20} 1.4862; d_4^{20} 1.5152; Found MR 55.90; Calculated 55.74.

B. A mixture of 21 g of (V) and 0.5 g of aluminum chloride was distilled at atmospheric pressure. The yield of (XVI) was 13 g (68.4%).

1,1- and 1,2-Bistrimethylsilylethylenes $(CH_3)_3SiCH=CHSi(CH_3)_3$ and $(CH_3)_3SiC(Si(CH_3)_3)=CH_2$ (XVII)

To a solution of methylmagnesium bromide prepared from 29 g of magnesium in 300 ml of ether, 59 g of (XVI) was added. On the next day the contents of the flask were boiled for seven hours. The mixture was decomposed with dilute hydrochloric acid, and distillation of the ether layer (dried with calcium chloride) through a column gave 16 g (46.5%) of (XVII), b.p. 145-148°; m.p. about −70°; n_D^{20} 1.4337; d_4^{20} .7702; Found MR 58.24; Calculated MR 57.96.

Found %: C 55.70; 55.80; H 11.70; 11.80; Si 32.27; 32.42
$C_8H_{20}Si_2$. Calculated %: C 55.74; H 11.69; Si 32.55

Δ ν (cm^{-1}): 225 (4), 321 (5), 418 (0), 472 (6), 548 (0), 608 (7), 646 (0), 695 (6), 830 (2), 845 (2), 1189

* The synthesis of (XV) was carried out by Glukhovtsev [16].

(3), 1253 (4), 1295 (1), 1404 (4), 1420 (4), 1570 (b), 2980 (10), 2967 (10), 3016 (2).

Thus the spectrum of (XVII) contains the frequencies of the compounds (XIV) and (XV), the most intense being: (XIV), 321, 608, 845, 1295, 1570; (XV), 472, 646, 830, 1404, 3016. In the infrared spectrum of (XVII) a band at 3.328 μ (3014 cm^{-1}) was observed; this characterizes unsymmetrical vibrations in the $=CH_2$ group. This frequency is absent in the spectrum of (XIV), but is very distinct in that of (XV).

Trichloropropenylsilane $CH_3CH=CHSiCl_3$ (XVIII)

A mixture of 87 g of trichloro(2-chloropropyl)silane [17] and 63 g of quinoline was distilled at the usual rate. Redistillation through a column gave 44 g (61%) of (XVIII), b.p. 123-126° and n_D^{20} 1.4513. The literature [5] gives b.p. 126° and n_D^{20} 1.4513.

Trichloro(2-methylpropenyl)silane $(CH_3)_2C=CHSiCl_3$ (XIX)

A mixture of 28 g of (III) and 19 g of quinoline gave 18 g (76.5%) of (XIX), b.p. 153° (739 mm); n_D^{20} 43.04. For trichloro (2-methylallyl) silane the literature [18] gives b.p. 140-141° (743 mm), n_D^{20} 1.4505; d_4^{20} 1.1784.

SUMMARY

1. The dehydrochlorination of the following compounds was carried out for the first time:

With the aid of quinoline: $Cl_3SiCH_2CHClCH_3$, $Cl_3SiCH_2CCl(CH_3)_2$ and $Cl_3SiCHClCH_2SiCl_3$.

With the aid of aluminum chloride: 1,1- 1,2- and 2,2-dichloroethyltrichlorosilanes, $Cl_3SiCH_2CH(CH_3)CH_2Cl$ and $Cl_3SiCHClCH_2SiCl_3$.

2. It was shown that, when quinoline was used, dehydrochlorination products were obtained in high yield only when the chlorine atom was in the β-position with respect to silicon, the products being exclusively 1-alkenylsilanes. Aluminum chloride can be applied for dehydrochlorination only in the case of trichloro(chloroalkyl)silanes, but the chlorine atom may be in the α-, β-, or γ-position.

3. A new arrangement in organosilicon chemistry was discovered.

In the dehydrochlorination of 1-chloro-1,2-bistrichlorosilylethane (1,1,1,2,4,4,4-heptachloro-1,4-disilabutane) with quinoline, only 1,2-bistrichlorosilylethylene was formed, whereas in dehydrochlorination with aluminum chloride the same product was obtained in admixture with 1,1-bistrichlorosilylethylene. A scheme is given in which an isomeric change in the skeleton of the original compound occurs in the course of the dehydrochlorination.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 9. CONDENSATION OF 1-VINYL-1-CYCLOHEXENE WITH METHYL ACRYLATE

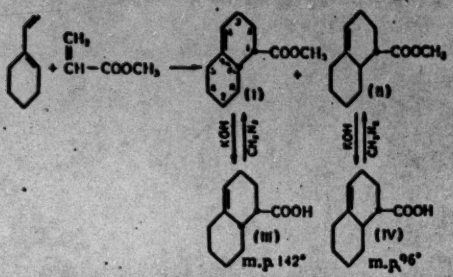
I. N. Nazarov, V. F. Kucherov, and G. M. Segal

It has now been established beyond doubt that diene condensations between monosubstituted dienes and unsymmetrical dienophiles can result in the formation of different stereoisomers, the relative amounts of which depend on the reaction temperature. In the condensation of 1-phenyl-1, 3-butadiene [1] and of trans-piperylene [2] with acrylic acid and its derivatives it was found, for the first time, that such diene syntheses can proceed in two sterically different directions a and b, and the amount of the trans-adduct, formed according to scheme b, increases with rise of temperature.

This relationship was established most clearly in a study of the condensation of trans-2,4-pentadienoic acid with acrylic acid [3]. Trans- adducts were obtained also in the reaction between various disubstituted 1,3-butadienes and acrylic acid [4], and also in the dimerization of 1-phenyl-1,3-butadiene [5] and its condensation with itaconic anhydride [6].

In our laboratory the formation of stereoisomers in diene syntheses with more complex polycyclic systems was observed in the condensation of various vinylcycloalkenes with α,β-unsaturated ketones [7]. We made our most detailed studies of the stereochemistry of the diene synthesis for the condensation of maleic and citraconic anhydrides with 1-vinyl-1-cyclohexene [8], and for the condensation of citraconic anhydride with 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene [9]. In these studies we established interesting stereochemical regularities in the behavior of o-dicarboxylic cyclic acids, particularly with respect to the steric selectivity of hydrogenation.

With the object of making a further study of the stereochemistry of hydrogenation and the steric directivity of the diene synthesis, we made a detailed study of the condensation of 1-vinyl-1-cyclohexene with methyl acrylate. A study of the reaction under different conditions showed that in this diene condensation a mixture of isomeric 1,2,3,5,6,7,8,8a-octahydro-1-naphthoic esters (I) and (II) is formed, the relative amounts of which being greatly dependent on temperature:



Hydrolysis of the mixture of esters (I) and (II) gave a mixture of the corresponding acids, and from this mixture, submitted to fractional crystallization, we succeeded in isolating the individual syn- and anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acids (III) and (IV) *, the relative amounts of which are shown in the in their dependence on the temperature of the diene condensation.

TABLE

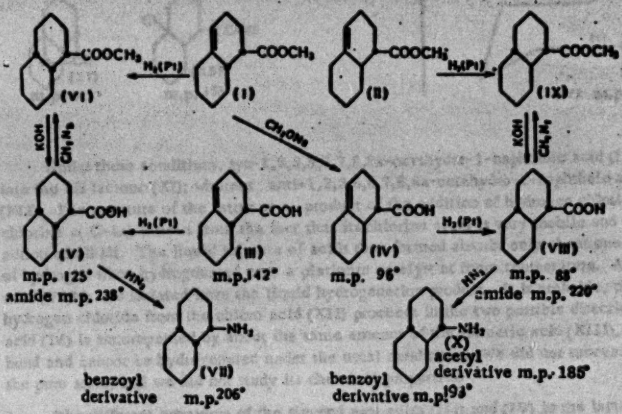
Temperature (°C) and duration of condensation	Yield of adduct (%)	Amount (%) isolated after hydrolysis	
		of acid (III)	of acid (IV)
20°; 45 days	20	52	Not isolated
50°; 70 hours	16	52	8
80°; 24 hours	70	34	15
170°; 6 hours	98	26	32

At 50° the condensation of 1-vinyl-1-cyclohexene with methyl acrylate is very slow: after 70 hours a yield of about 16% of a liquid mixture of the esters (I) and (II) was obtained, and from this, after hydrolysis and crystallization, we isolated 52% of syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III), m.p. 142°, and only 8% of anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV), m.p. 96°. At 170° 1-vinyl-1-cyclohexene condenses very rapidly with methyl acrylate: after six hours a 96% yield was obtained of a mixture of the esters (I) and (II), and from this, after hydrolysis and crystallization, we isolated only 26% of the syn acid (III), whereas the yield of the anti acid (IV) was now 32%. The rest of the acid remained in the form of a liquid mixture of isomers. The separation of the isomeric liquid esters (I) and (II) does not appear to be feasible, and they were prepared in the pure state by esterifying the pure crystalline acids (III) and (IV) with diazomethane. The increase in the amount of the anti isomer (IV) with rise in the temperature of the diene condensation is not associated with the thermal isomerization of the syn isomer (I), for this ester is not converted into the corresponding anti isomer (II) when heated at 230° for two hours: when the product is hydrolyzed, more than 50% of the original syn acid (III) is recovered and about 20% of a crystalline substance of undetermined structure, m.p. 184-185°, is obtained.

In order to prove that the isomeric esters (I) and (II), and also the corresponding acids (III) and (IV), are epimers with respect to hydrogen at C-8a, we have investigated their isomerization and hydrogenation, which made it possible to pass, after replacement of carboxyl by amino, to the known decahydro-1-naphthylamines, the spatial configurations of which have been established. It was found that methyl syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoate (I) was isomerized to anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV) in good yield when boiled with sodium methoxide in methanol. Under similar conditions methyl anti-1,2,3,5,6,7,8,8a-octahydro-1-napthoate (II) did not isomerize at all, since the hydrogen atoms at C-1 and C-8a in this compound are already in the trans configuration. It was thus established that the ester (I) and the acid (III) are indeed syn isomers having a cis arrangement of the hydrogens at C-1 and C-8a, whereas the ester (II) and the acid (IV) belong to the anti series and have a trans arrangements of the hydrogens at C-1 and C-8a.

* The nomenclature and representation of stereoisomers are based on those for tetradecahydrophenanthrene [10].

The isomeric syn and anti acids (III) and (IV), and also the corresponding esters (I) and (II), are readily hydrogenated over a platinum catalyst under the usual conditions, which indicates the normal 4-position of the double bond, corresponding to the normal scheme of the diene synthesis. The characteristic feature of this hydrogenation is its strict steric selectivity, which we have pointed out previously [8]: as a result, only one of the possible stereoisomers is formed. It was found that hydrogenation of syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III) gave cis-syn-decahydro-1-naphthoic acid (V), m.p. 125°, identical with the substance previously assigned this formula [11]. The same acid was formed by hydrolysis of the cis-syn ester (VI), which was obtained by hydrogenation of the syn ester (I). In order to provide further confirmation of the spatial configuration of the cis-syn acid (V), it was converted with the aid of sodium azide (Schmidt reaction) into the known cis-syn-decahydro-1-naphthylamine (VII), identified as the benzoyl derivative [12].

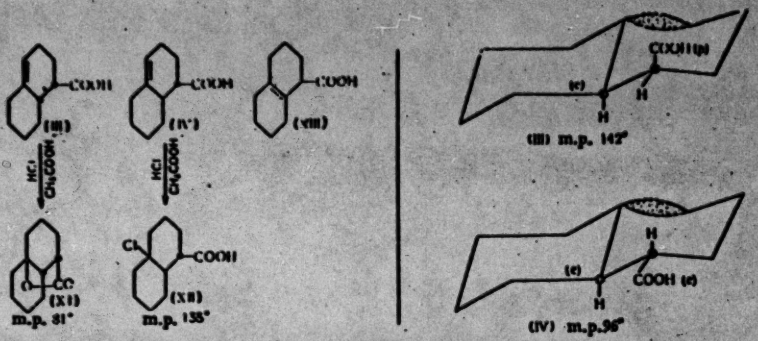


These results completely confirm the configuration of the syn acid (III) and prove that in its hydrogenation, and also in the hydrogenation of the ester (I), addition of hydrogen proceeds selectively from the side opposite to the carboxy group (less screened). Only in this case will the saturated acid (V) have a cis-syn configuration with the equatorial disposition of the carboxyl, which accounts for the inability of its ester (VI) to undergo isomerization under the action of sodium methoxide.

Similar transformations were carried out also on the isomeric anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV). Its hydrogenation over a platinum catalyst gave the individual trans-anti-decahydro-1-naphthoic acid (VIII), m.p. 88° (amide, m.p. 220-221°), which was formed also by the hydrolysis of the saturated ester (IX) obtained by hydrogenation of the anti ester (II). The trans-anti configuration of the saturated acid (VIII) is proved quite reliably by the fact that treatment with sodium azide in accordance with the Schmidt reaction converts it into the known trans-anti-decahydro-1-naphthylamine (X), identified by the melting points of its acetyl and benzoyl derivatives [12]. It follows that the hydrogenation of (II) and (IV) also proceeds from the side opposite to the carboxyl and results in the formation of the acid (VIII) and the ester (IX), which belong to the trans-decahydronaphthalene series.

For trans-anti-decahydro-1-naphthoic acid (VIII) the literature [11] gives m.p. 102°, but the constants of its derivatives (amide and decahydro-1-naphthylamine) are identical with our values. The fact that the amide of m.p. 220-221° can be reconverted in high yield into the trans-anti acid (VIII) of m.p. 88° (and not 102°) shows that the previously described method [11] of preparing trans-anti-decahydro-1-naphthoic acid (VIII) was not stereospecific, and the acid of m.p. 102° contained the cis-syn acid (V) as impurity. This is confirmed by the fact that artificially prepared mixtures of the isomeric acids (V) and (VIII) have sharp melting points in the range 90-120° (the actual value depending on the relative amounts of the acids) and, for practical purposes, cannot be separated by crystallization.

The isomeric acids (III) and (IV) react quite differently with hydrogen chloride in glacial acetic acid.



Under these conditions, syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III) is converted quantitatively into the cis-lactone (XI), whereas anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV) gives the chloro acid (XII). The structure of the latter as a product of the addition of hydrogen chloride at the double bond (with chlorine at C-4a) follows from the fact that its chlorine atom is very mobile and is readily eliminated by the action of alkali. The liquid mixture of acids then formed absorbs only about one-half of a molecular equivalent of hydrogen when hydrogenated over a platinum catalyst at room temperature. A small amount of the trans-anti acid (VIII) was isolated from the liquid hydrogenation product. It is probable, therefore, that elimination of hydrogen chloride from the chloro acid (XII) proceeds in the two possible directions, so that the original anti acid (IV) is accompanied by about the same amount of the isomeric acid (XIII), which has an intercycle double bond and cannot be hydrogenated under the usual conditions. We did not succeed in isolating the acid (XIII) in the pure state, and we did not study its chemical properties.

The different behaviors of the syn and anti acids (III) and (IV) in the lactonization reaction and the above-discussed selective hydrogenation of these acids into acids of the cis- and trans-decahydronaphthalene series can be explained in a graphic manner by reference to molecular models *.

It follows quite obviously from these models that the syn acid (III) should have a high tendency to undergo lactonization and should give only cis-syn-decahydro-1-naphthoic acid (V) when hydrogenated, owing to addition of hydrogen from the least screened side. Unlike the syn acid, the anti acid (IV) gives trans-anti-decahydro-1-naphthoic acid (VIII) when hydrogenated, and it is incapable of undergoing lactonization, but can readily undergo addition of hydrogen chloride at the double bond.

EXPERIMENTAL

Condensation of 1-Vinyl-1-cyclohexene with Methyl Acrylate

a) A solution of 70 g (40% excess) of 1-vinyl-1-cyclohexene and 40 g of methyl acrylate in 70 ml of dry benzene was boiled in presence of a little pyrogallol for 24 hours. Benzene was distilled off, and vacuum distillation of the residue gave 61.5 g (70% on the methyl acrylate) of liquid adduct, b.p. 125-127° (10 mm) and n_D^{19} 1.4960.

Found %: C 74.50; 74.48; H 9.31; 9.41
$C_{12}H_{18}O_2$. Calculated %: C 74.14; H 9.34

The adduct was hydrolyzed by boiling it with 185 ml of 20% caustic potash solution until solution was complete. The solution was filtered and acidified with hydrochloric acid. The oil that separated partially crystal-

* The symbol (e) denotes an equatorial disposition of a substituent, and the symbol (p) a polar disposition.

lized after one day. The crystals were pressed on the filter to remove oil and were washed several times with petroleum ether. The product, amounting to 25.4 g, melted at 137-139°. Crystallization from a 2 : 1 mixture of diethyl ether and petroleum ether gave 19.7 g (34.5%) of pure syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III), m.p. 141-142°.

Found %: C 73.0; 72.94; H 8.80; 8.95
$C_{11}H_{16}O_2$. Calculated %: C 73.29; H 8.95

The amide of the syn acid (III), which was prepared as usual through the acid chloride, melted after crystallization from ethanol at 218-219°.

Found %: C 73.72; 73.68; H 9.53; 9.56; N 7.57; 7.65
$C_{11}H_{17}NO$. Calculated %: C 73.74; H 9.49 N 7.82

The solution remaining after the separation of the syn acid (III) was evaporated to low bulk and set aside at 0° for two days. The crystals that separated were filtered off, the product (5.5 g) being the isomeric anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV), m.p. 95-97°. Vacuum distillation of the liquid residue gave 21 g of a liquid mixture of acids, b.p. 134-136° (1.5 mm), from which a further 3.5 g of the anti acid (IV), m.p. 91-95°, was isolated by dissolving the mixture in petroleum ether and cooling the solution in a freezing mixture. Crystallization from petroleum ether gave 8.7 g (15.3%) of anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV) of constant melting point (96-97°).

Found %: C 73.42; 73.48; H 9.07; 8.85
$C_{11}H_{16}O_2$. Calculated %: C 73.29; H 8.95

The amide of the anti acid (IV), which was prepared in the usual way, had m.p. 202-203° (from ethanol).

Found %: C 73.58; 73.49; H 9.41; 9.53
$C_{11}H_{17}NO$. Calculated %: C 73.74; H 9.49

The residue from the separation of the crystalline isomers was vacuum-distilled and gave 17.6 g of a thick liquid, b.p. 135-137° (2 mm). Very slow partial crystallization occurred. The substance was not investigated further.

b) A solution of 10 g of 1-vinyl-1-cyclohexene, 5.7 g of methyl acrylate, and 0.1 g of pyrogallol in 10 ml benzene was set aside at room temperature for 45 days. Benzene was distilled off, and vacuum distillation of the residue was 2.5 g of a liquid adduct, b.p. 124-125° (11 mm) and n_D^{25} 1.4956. The product was hydrolyzed at the boil with 12 ml of 20% caustic potash solution (three hours) and the solution was acidified with hydrochloric acid. The liquid acids so obtained crystallized partially when allowed to stand. The crystals were washed on the filter with a little petroleum ether. The solid product, amounting to 1.2 g (51.7%), was syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III), m.p. 139-141°, identical with the product obtained in the preceding experiment. Owing to its small amount, the liquid product was not investigated.

c) A solution of 31.8 of 1-vinyl-1-cyclohexene, 18.1 g of methyl acrylate, and 0.1 g of pyrogallol in 35 ml of benzene was heated at 50° for 70 hours. Vacuum distillation gave 6.6 g of adduct, b.p. 126-128° (12 mm) and n_D^{25} 1.4940, and this, by hydrolysis, treatment as before, and crystallization from a 2 : 1 mixture of diethyl ether and petroleum ether, gave 3.2 g of pure syn acid (III), m.p. 141-142°. The mother liquor, after evaporation, dissolution in a little petroleum ether, and freezing, gave 0.7 g of a crystalline mixture melting at 90-92°. Crystallization of this from petroleum ether gave 0.5 g of anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV), m.p. 96-97°, identical with the product obtained in the first experiment.

d) A solution of 10 g of 1-vinyl-1-cyclohexene and 5.7 g of methyl acrylate in 10 ml of benzene was heated in presence of pyrogallol in a metal ampoule at 170° for six hours. Vacuum distillation gave 12.9 g (98%) of a liquid adduct, b.p. 118-120° (9 mm) and n_D^{17} 1.4970. This, after hydrolysis and treatment as before gave 3.1 g (20%) of the syn acid (III), m.p. 140-141°. From the mother liquor, after two freezing treatments,

4.0 g of crystals, m.p. 90-92°, was obtained; crystallization of these from petroleum ether gave 3.7 g (32%) of pure anti acid (IV), m.p. 95-96°.

Methyl syn-1,2,3,5,6,7,8,8a-Octahydro-1-naphthoate (I)

A solution of 5 g of syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III), m.p. 141-142°, was treated with an ethereal solution of diazomethane. Vacuum distillation gave 5.0 g of the syn ester (I), b. p. 124-125° (9 mm); n_D^{20} 1.4960; d_4^{20} 1.0450; Found MR 54.22; Calculated MR 54.65.

Found %: C 73.92; 74.07 H 9.47; 9.29
$C_{12}H_{18}O_2$ Calculated %: C 74.14; H 9.34

Hydrolysis of the syn ester (I) with boiling 20% caustic potash solution gave a good yield of the original syn acid (III), m.p. 140-141°.

Methyl anti-1,2,3,5,6,7,8,8a-Octahydro-1-naphthoate (II)

In a similar way, 6 g of anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (IV), m.p. 96-97°, was treated with an ethereal solution of diazomethane, and distillation gave 6.1 g of the anti ester (II), b.p. 120° (9 mm) n_D^{20} 1.4945; d_4^{20} 1.0380; Found MR 54.48; Calculated MR 54.67.

Found %: C 74.02; 74.25; H 9.23; 9.31
$C_{12}H_{18}O_2$ Calculated %: C 74.14; H 9.34

Hydrolysis of the anti ester (II) gave a quantitative yield of the original anti acid (IV), m.p. 95-96°.

Isomerization of Methyl syn-1,2,3,5,6,7,8,8a-Octahydro-1-naphthoate (I)

Methyl syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoate (I) (6.0 g) was added to a solution of 18 g of sodium in 400 ml of absolute methanol, and the mixture was boiled for 18 hours. Methanol was distilled off under reduced pressure, and 130 ml of water was added to the residue. After being boiled for three hours, the mixture was filtered and then carefully acidified to Congo red with hydrochloric acid. Product was 5.4 g of an acid of m.p. 90-92°, and crystallization from petroleum ether gave 4.7 g (84.5%) pure anti-1,2,3,5,6,7,8,8a-octahydro--1naphthoic acid (IV), m.p. 96-97°, undepressed by admixture of sample prepared by hydrolysis of the diene-synthesis products.

cis-syn-Decahydro-1-naphthoic Acid (V)

The syn acid (III) (4.4 g) was dissolved in methanol (40 ml) and hydrogenated over platinum oxide. One molecular equivalent of hydrogen (600 ml, 20°) was absorbed. After removal of catalyst, distillation of the methanol, and washing of the crystalline residue with petroleum ether, 4.2 g of the known cis-syn acid (V), m.p. 123-125°, was isolated (the literature gives m.p. 125°). The amide prepared from this acid in the usual way melted after crystallization from ethanol at 238-239° (the literature gives m.p. 238°).

Methyl cis-syn-Decahydro-1-naphthoate (VI)

The syn ester (I) (5 g) was dissolved in methanol (25 ml) and hydrogenated over a platinum catalyst. One molecular equivalent of hydrogen (690 ml. 20°) was absorbed. Distillation gave 4.7 g of the cis-syn methyl ester (VI), b.p. 123-124° (9 mm); n_D^{20} 1.4825, d_4^{20} 1.0180; Found MR 54.95; Calculated MR 54.87.

Found %: C 73.24; 73.12; H 10.08; 9.96
$C_{12}H_{20}O_2$ Calculated %: C 73.42; H 10.21

The same cis-syn ester (VI) was prepared in quantitative yield by treating the cis-syn acid (V), m.p. 125°, with diazomethane. Hydrolysis of the cis-syn ester (VI) with boiling 20% caustic potash solution gave a yield of about 90% of the pure original cis-syn acid (V), m.p. 124-125°.

cis-syn-Decahydro-1-naphthylamine (VII)

Concentrated sulfuric acid (17.5 ml) was added to a solution of 1.6 g of the cis-syn acid (V), m.p. 124–125°, in 44 ml of chloroform, the mixture was heated to 40°, and 1 g of sodium azide was added gradually with vigorous stirring. Stirring was continued at 50° for 90 minutes, and the mixture was cooled and poured into 50 ml of water. The aqueous layer was separated, extracted with ether, and saturated with caustic soda. The amine that separated was extracted with ether, the ether layer was dried with sodium sulfate, and the ether was distilled off. The cis-syn-decahydro-1-naphthylamine (VII) so obtained was benzoylated in the usual way by addition of 2 ml of benzoyl chloride and 30 ml of 5% caustic soda solution. A product (1.7 g) of m.p. 190–195° was obtained, and one crystallization of this from ethanol gave 1.2 g of pure N-(cis-syn-decahydro-1-naphthyl) benzamide, m.p. 206-207°, which is in accord with data in the literature [12].

trans-anti-Decahydro-1-naphthoic Acid (VIII)

The anti acid (IV) of m.p. 97° (4.8 g) was dissolved in methanol (30 ml) and hydrogenated over platinum oxide. One molecular equivalent of hydrogen was absorbed. The crystalline hydrogenation product (4.8 g), which was isolated after removal of catalyst and solvent, melted at 75-78°. Crystallization from low-boiling petroleum ether gave 3.3. g of pure trans-anti-decahydro-1-naphthoic acid (VIII), which had a constant melting point of 87-88°. Repeated crystallization from petroleum ether or aqueous methanol did not effect its melting point.

Found %: C 72.23; 72.36; H 9.99; 9.98
$C_{11}H_{18}O_2$. Calculated %: C 72.49; H 9.96

Amide of the Acid (VIII)

Oxalyl chloride (2 ml) was added to a solution of 2.4 g of the trans-anti acid (VIII), m.p. 87-88°, in 25 ml of absolute benzene and the mixture was heated at 30° for 45 minutes. Benzene and excess of oxayl chloride were removed under reduced pressure, and the residue—an ethereal solution of the acid chloride—was added with stirring to 10 ml of aqueous ammonia at 0°. The product was 2.3 g of the amide of the trans-anti acid (VIII), m.p. 214-216°, and after crystallization from a 2 : 1 mixture of ethanol and chloroform it had a constant melting point of 220-221°, which is in accord with the literature [11] (m.p. 222°).

In order to reconvert the product into the trans-anti acid (VIII), a mixture of 0.5 g of amide, m.p. 220–221°, and 3 ml of concentrated sulfuric acid was cooled to 0°, and a solution of 1.7 g of sodium nitrite in 8 ml of water was added gradually with stirring, the mixture then being heated over 15 minutes at 60° and poured into 30 ml of ice water. The precipitate that formed was filtered off, washed with water, and dissolved in 10 ml of 5% caustic soda solution. The solution was filtered, and acidification gave 0.45 g of crystalline acid (VIII), which after being washed with water and dried had m.p. 86-87.5° undepressed by admixture of the above-described sample.

Methyl trans-anti-Decahydro-1-naphthoate (IX)

The anti ester (II) (2.9 g) was dissolved in methanol (20 ml) and hydrogenated over a platinum catalyst. One molecular equivalent of hydrogen (380 ml, 20°) was absorbed. Distillation gave 2.7 g of the trans-anti ester (IX), b.p. 118–119° (9 mm) n_D^{20} 1.4778, d_4^{20} 1.0160; Found MR 54.62; Calculated MR 54.87

Found %: C 73.19; 73.27; H 10.24; 10.19
$C_{12}H_{20}O_2$. Calculated %: C 73.42; H 10.21

Hydrolysis of the trans-anti ester (IX) so obtained gave an 80% yield of pure original trans-anti acid (VIII), m. p. 86–88°.

trans-anti-Decahydro-1-naphthylamine (X)

By the reaction already described, 2.4 g of the trans-anti acid (VIII), m.p. 86-88°, gave 1.5 g of trans-anti-decahydro-1-naphthylamine (X). Benzoylation of 0.7 g of this amine by the usual method and crystallization of the product gave 0.75 g of N-(trans-anti-decahydro-1-naphthyl) benzamide, m.p. 192-193° (the

literature [11] gives 195°). In order to acetylate the amine, a solution of 0.7 g of (X) in 7 ml of absolute benzene and 7 ml of acetic anhydride was boiled for 90 minutes. The solution was evaporated to dryness, and the crystalline residue was washed on the filter with petroleum ether. The product was 0.55 g of N-(trans-anti-decahydro-1-naphthyl) acetamide, which was crystallized from petroleum ether (b.p. 50-70°), and then melted at 185-186° (the literature [11] gives m.p. 182°.

cis Lactone (XI)

A solution of 2 g of syn-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid (III) in 20 ml of glacial acetic acid was saturated with dry hydrogen chloride and heated for one hour at 60°. Acetic acid was distilled off under reduced pressure. Washing of the crystalline residue on the filter yielded 1.2 g of the cis lactone (XI), m.p. 78-79°. We succeeded in isolating a further 0.35 g of cis lactone, m.p. 76-78° from the mother liquor. After crystallization from a 1 : 3 mixture of diethyl ether and petroleum ether, the pure cis lactone (XI) had m.p. 80-81°.

Found %: C 73.52; 73.40; H 8.87; 9.04
$C_{11}H_{16}O_2$. Calculated %: C 73.29; H 8.95

Chloro Acid (XII)

A solution of 3 g of anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid in 30 ml of glacial acetic acid was saturated with dry hydrogen chloride and heated for one hour at 60°. Acetic acid was distilled off under reduced pressure, and the crystalline residue was washed on the filter with petroleum ether. The product was 2.2 g of the chloro acid (XII), m.p. 147-149°, which, after being crystallized from a 1 : 1 mixture of diethyl ether and petroleum ether, had a constant melting point of 154-155°.

Found %: C 61.33; 61.16 H 7.88; 7.82; Cl 17.0
$C_{11}H_{17}O_2Cl$. Calculated %: C 61.32; H 7.87; Cl 16.35

A solution of 4 g of the chloro acid (XII) in 40 ml of 5% caustic soda solution was boiled for five minutes, and then acidified. The oil that separated was extracted with ether. Vacuum distillation gave 3.2 g of a liquid mixture of acids, b.p. 132-134° (2 mm), n_D^{20} 1.5115. When this mixture was hydrogenated in methanol over a platinum catalyst, only 0.5 of a molecular equivalent of hydrogen was absorbed, after which hydrogen came to a complete stop. Methanol was distilled off under reduced pressure, and the liquid residue (n_D^{20} 1.5050) was dissolved in the minimum amount of petroleum ether. On standing, the solution gave 0.2 g of trans-anti-decahydro-1-naphthoic acid (VIII), m.p. 83-85°, undepressed by admixture of a sample obtained in a previous experiment (above).

SUMMARY

1. A study was made of the condensation of 1-vinyl-1-cyclohexene with methyl acrylate. Hydrolysis of the product gives a mixture of syn- and anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acids (III) and (IV), and it was shown that with rise in the condensation temperature the amount of the anti isomer (IV) increases with simultaneous decrease in the amount of the syn isomer (III).

2. The spatial configurations of syn- and anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acids (III) and (IV) were established by converting them into known decahydro-1-naphthylamines; they are epimers with respect to the hydrogen at C-8a.

3. It was shown that the hydrogenation of the isomeric acids (III) and (IV), and also of the corresponding esters (I) and (II), is sterically selective and occurs from the side opposite to the carboxyl with formation of acids (V) and (VIII), and also esters (VI) and (IX), of the cis- and trans-decahydronaphthalene series respectively.

4. It was shown that the isomeric syn and anti acids (III) and (IV) behave differently under lactonization conditions. An examination of molecular models has enabled us to explain the stereochemical peculiarities of the epimers that we have obtained.

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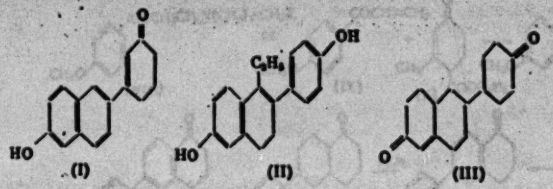
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION 37. SYNTHESIS OF STERIOD ANALOGS NOT CONTAINING A B RING

I. N. Nazarov and S. I. Zavyalov

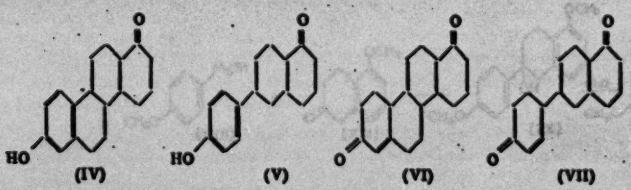
In recent years data have been reported on the hormone activity of some compounds of the 2-phenylnaphthalene type (I) [1], (II) [2], and (III) [3], which can be regarded as structural analogs of steroid hormones in which the C rings have been removed:



(I) (II) (III)

In this connection it appeared to be of interest also to investigate the effect on the hormone activity of the absence of the B ring in the molecules of estrone, androsterone, and related substances.

With this object we decided to synthesize compounds of the types (V) and (VII), which can be regarded as analogs of 13-nor-D-homoestrone (IV) and 18, 19-bisnor-D-homo-4-androsten-3,17-dione (VI), from which their structures are obtained by removal of the B rings.



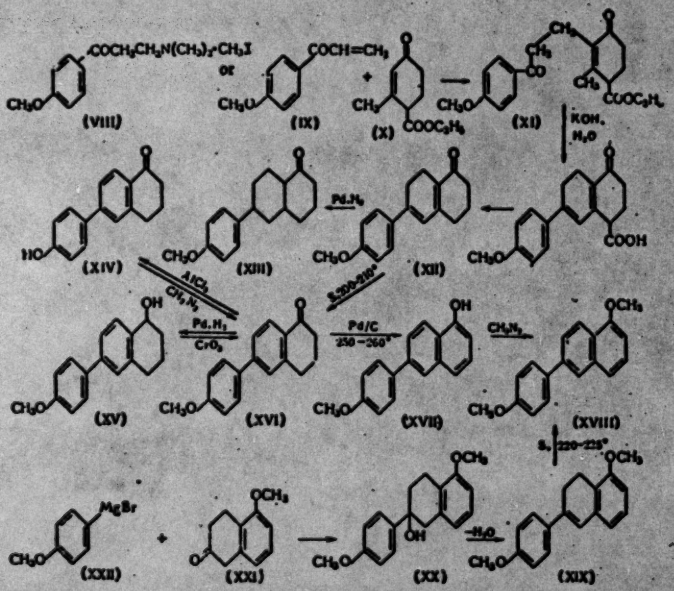
(IV) (V) (VI) (VII)

Reaction of the methiodide of 3-dimethylamino-4'-methoxypropiophenone (VIII) or of 4'-methoxyacrylophenone (IX) with the sodium derivative of ethyl 2-methyl-4-oxo-2-cyclohexene-1-carboxylate (Hagemann's ester) (X) in methanol solution gave the corresponding addition product (XI), which, without isolation in the pure state, was treated successively with boiling aqueous-methanolic caustic potash and dilute hydrochloric acid. In these

treatment, as a result of an intramolecular condensation of the crotonic type, hydrolysis, decarboxylation and partial dehydrogenation, a mixture was formed of 3,4,7,8-tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII) and 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI), which are steroid analogs without D rings.

In order to prove the structures of these ketones, some of their physical properties were examined and 2--phenylnaphthalene derivatives obtained from them were identified with compounds synthesized independently. When heated with sulfur at 200-210° for a short time, the methoxy ketone (XII) was readily dehydrogenated to the 3,4-dihydro-1(2H)-naphthalenone (XVI), which was completely aromatized at a higher temperature (250-260°) in presence of palladized charcoal to the corresponding 1-naphthol derivative (XVII). When hydrogenated in methanol solution over a palladium catalyst, the methoxy ketone (XII) absorbed two molecular proportions of hydrogen and gave the octahydro-1(2H)-naphthalenone (XIII). Under the same conditions the dihydro-1(2H)--naphthalenone (XVI) was reduced to the tetrahydro-1-naphthol (XV), oxidation of which with chromic anhydride in acetic acid gave the original dihydro-1(2H)-naphthalenone (XVI).

Demethylation of the methoxy ketone (XVI) by means of aluminum chloride in boiling xylene gave a high yield of the phenol (XIV), which was reconverted by diazomethane in ethereal-methanolic solution into the original methoxy ketone (XVI). In the demethylation of the dienone (XII) under the same conditions, partial aromatization occured, and apart from a small amount of the phenol (XIV), we were unable to isolate any pure substances.



The 1-naphthol derivative (XVII) was converted by the action of diazomethane into 1-methoxy-8-p--methoxyphenylnaphthalene (XVIII), which we synthesized independently from 3,4-dihydro-5-methoxy-2(1H)--naphthalenone (XXI). Reaction of the last compound with p-methoxyphenylmagnesium bromide (XXII) followed by dehydration of the alcohol (XX) gave 1,2-dihydro-8-methoxy-3-p-methoxyphenylnaphthalene (XIX), which was dehydrogenated with sulfur at 220-225° into the diether (XVIII) referred to above.

The distribution of double bonds in the molecule of the dienone (XII) is in full accord with its ultraviolet spectrum • (Curve 1), which has two maxima at 372 mμ (ε $1.50 \cdot 10^4$) and 317 mμ (ε $1.11 \cdot 10^4$). The calculated absorption maximum of the dienone (XII) (374 mμ) agrees closely with the experimental results. The hypsochromic shift in the maximum which occurs when we pass to the 3,4-dihydro-1(2H)-naphthalenone (XVI) (Curve 2; λ_{max} 311 mμ; ε $3.33 \cdot 10^4$) indicates the lower degree of conjugation in the molecule of this ketone.

Reduction of the tricyclic anisole derivatives (XII), (XIII), and (XIX) by means of lithium in liquid ammonia [5] opens the way to the preparation of a series of hydroaromatic steroid analogs of the type (VII).

EXPERIMENTAL

Methiodide of 3-Dimethylamino-4'-methoxypropiophenone (VIII). The hydrochloride of 3-dimethylamino-4'-methoxypropiophenone (25 g, m.p. 180-181°) [6] was added in portions to an ice-cooled, stirred mixture of 25 g of caustic potash, 150 ml of water, and 700 ml of ether. When the precipitate had redissolved, the ether layer was separated, and 44 g of methyl iodide was added to it. In the course of 12 hours at room temperature, 74 g (76%) of the methiodide of 3-dimethylamino-4'-methoxypropiophenone (VIII) was precipitated; it melted with decomposition at 178-181°.

Found %: I 36.18; 36.02

$C_{13}H_{20}O_2NI$. Calculated %: I 36.4

4'-Methoxyacrylophenone (IX). The methiodide of 3-dimethylamino-4'-methoxypripiophenone (VIII) (6 g) was heated at a bath temperature of 235-240° at a pressure of 1 mm. The product was 2.1 g (78%) of 4'-methoxyacrylophenone (IX), b.p. 128-131° (1 mm) and n_D^{20} 1.5820 [6].

Reaction of the Methiodide of 3-Dimethylamino-4'-methoxypropiophenone with the Sodium Derivative of Ethyl 2-Methyl-4-oxo-2-cyclohexene-1-carboxylate. The methiodide of 3-dimethylamino-4'-methoxypropiophenone (VIII) (74 g) was added gradually to an ice-cooled, stirred methanol solution of the sodium derivative prepared from 38 g of ethyl 2-methyl-4-oxo-2-cyclohexene-1-carboxylate (X) (b.p. 113-118° at 1 mm) and n_D^{20} 1.4880 [7], 4.5 g of sodium, and 100 ml of methanol. The mixture was stirred for four hours at room temperature. Methanol was then distilled off under reduced pressure, and the residue was treated with 100 ml of water and extracted with chloroform. A yield of 57 g was obtained of the crude condensation product (XI), n_D^{20} 1.5630.

Condensation of Ethyl 2-Methyl-4-oxo-2-cyclohexene-1-carboxylate with 4'-Methoxyacrylophenone. Ethyl 2-methyl-4-oxo-2-cyclohexene-1-carboxylate (X) (2.7 g) was added to an ice cooled, stirred solution of sodium methoxide prepared from 0.05 g of sodium and 3 ml of methanol, and a solution of 2.1 g of 4'-methoxyacrylophenone (IX) in 3 ml of ether was then added. After 30 minutes at room temperature the solution was treated with 10 ml of dilute (1:5) hydrochloric acid and extracted with ether. A yield of 4.2 g of the crude condensation product (XI), n_D^{20} 1.5632, was obtained.

Preparation of 3,4,7,8-Tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone and 3,4-Dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone. A mixture of 57 g of the above described crude condensation product (XI), 20 g of caustic potash, 100 ml of water, and 300 ml of methanol was refluxed for three hours. After acidification to Congo red with concentrated hydrochloric acid, the solution was boiled for another ten minutes.

• The ultraviolet spectra were determined in methanol solution on a spectrophotometer having a Dianov-Klokov attachment.

The solution was evaporated down to one-third bulk under reduced pressure. Extraction of the residue with chloroform gave 34 g of an oil boiling at 230-240° (1 mm), and when ether was added to this there was a precipitate of 4.7 g of 3,4,7,8-tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII), m.p. 106-107° (from a mixture of benzene and heptane), λ_{max} (in methanol) 372 mμ (ε $1.50 \cdot 10^4$) and 317 mμ (ε $1.11 \cdot 10^4$).

Found %: C 80.20; 80.35; H 7.00; 7.16
$C_{17}H_{16}O_2$. Calculated %: C 80.3; H 7.1

After being washed with methanol its 2,4-dinitrophenylhydrazone melted at 224-226° with decomposition; λ_{max} (in methanol) 410 and 254 mμ.

Found %: N 12.95; 13.08
$C_{23}H_{22}O_5N_4$. Calculated %: N 12.90

A solution of 6 g of caustic potash in 50 ml of water and 280 ml of methanol was added to the mother liquor remaining after the isolation of the dienone (XII), and the mixture was refluxed for four hours. The above-described treatment gave 20 g of an oil of b.p. 225-240° (1 mm), and when ether was added to this there was a precipitate of 4.5 g of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI), m.p. 126-127° (from aqueous methanol); λ_{max} (methanol) 311 mμ (ε $3.33 \cdot 10^4$).

Found %: C 80.67; 80.62; H 6.33; 6.54
$C_{17}H_{16}O_2$. Calculated %: C 80.9 H 6.3

After being washed with methanol its 2,4-dinitrophenylhydrazone melted at 228-231° with decomposition.

Found %: N 13.18; 13.29
$C_{23}H_{20}O_5N_4$. Calculated %: N 12.9

From the mother liquor remaining after the separation of the dihydro-1(2H)-naphthalenone (XVI) a further 6 g of a crystalline mixture was precipitated, and by chromatography of this in ether on alumina, 2 g of dienone (XII) was isolated. Thus, the total yield of 3,4,7,8-tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII) was 6.7 g [12% on the methiodide of 3-dimethylamino-4'-methoxypropiophenone (VIII) taken].

Conversion of 3,4,7,8-Tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone into 3,4-Dihydro-6-p-methoxyphenyl 1(2H)-naphthalenone. A mixture of 0.5 g of 3,4,7,8-tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII) and 0.15 g of sulfur was heated at 200-210° for 30 minutes. By chromatography in ether on alumina, 0.25 g (50%) of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI), m.p 126-127°, was isolated.

Dehydrogenation of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone. A mixture of 0.9 g of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI) and 0.9 g of palladized charcoal (10% Pd) was heated at 259-260° for 20 minutes. The cooled reaction mixture was extracted with hot 5% caustic soda solution. Filtration and acidification with dilute hydrochloric acid gave 0.24 g (27%) of 6-p-methoxyphenyl-1-naphthol (XVII), m. p. 156-157° (from aqueous methanol).

Found %: C 81.45; 81.52; H 5.72; 5.83
$C_{17}H_{14}O_2$. Calculated %: C 81.6; H 5.6

Hydrogenation of 3,4,7,8-Tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone. 3,4,7,8-Tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII) (2.5 g) was hydrogenated in methanol over palladium supported on calcium carbonate and absorbed 238 ml (2 molecular equivalents) of hydrogen (20°, 753 mm). The product was 1.5 g (60%) of octahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XIII), b.p. 210-215° (1 mm) and n_D^{20} 1.5602

Found %: C 79.12; 79.28; H 8.25; 8.41
$C_{17}H_{22}O_2$. Calculated %: C 79.0 H 8.4

After being washed with methanol, its 2,4-dinitrophenylhydrazone melted with decomposition at 198-200°; λ_{max} (in methanol) 379 mμ (ε 1.06·10⁴).

Found %: N 12.95; 13.12

$C_{28}H_{28}O_5N_4$. Calculated %: N 12.8

Reduction of 3,4-Dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone. 3,4-Dihydro-6-p-methoxy-1(2H)-naphthalenone (XVI) (0.5 g) was hydrogenated in methanol at 20° and atmospheric pressure over palladium supported on calcium carbonate. The product was 0.2 g (40%) of 1,2,3,4-tetrahydro-6-p-methoxyphenyl-1-naphthol (XV), m.p. 95-97° (from a mixture of benzene and heptane).

Found %: C 80.58; 80.44; H 7.09; 7.07

$C_{17}H_{18}O_2$. Calculated %: C 80.3; H 7.1

Oxidation of 1,2,3,4-Tetrahydro-6-p-methoxyphenyl-1-naphthol. A mixture of 0.4 g of 1,2,3,4-tetrahydro-6-p-methoxyphenyl-1-naphthol (XV), 0.4 g of chromic anhydride, and 20 ml of glacial acetic acid was allowed to stand at room temperature for one day. Methanol (2 ml) was added, and solvents were distilled off under reduced pressure. The residue was treated with 10 ml of water and extracted with chloroform. Chromatography of the reaction products in ether on alumina gave 0.14 g (35%) of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI), m.p. 125-126°.

Demethylation of 3,4-Dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone. A mixture of 1 g of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI), 2 g of aluminum chloride, and 10 ml of dry xylene was boiled with stirring for five minutes. The cooled mixture was treated with ice and with dilute (1 : 1) hydrochloric acid. The phenol then precipitated was dissolved in hot 5% caustic soda solution, and the solution was filtered and again precipitated with hydrochloric acid. The product was 0.4 g (43%) of 3,4-dihydro-6-p-hydroxyphenyl-1(2H)-naphthalenone (XIV), m.p. 214-215° (from aqueous methanol).

Found %: C 80.67; 80.88; H 6.16; 6.12

$C_{16}O_2H_{14}$. Calculated %: C 80.67; H 5.9

Methylation of 3,4-Dihydro-6-p-hydroxyphenyl-1(2H)-naphthalenone. 3,4-Dihydro-6-p-hydroxphenyl-1(2H)-naphthalenone (XIV) (0.2 g) was dissolved in methanol (10 ml), excess of ethereal diazomethane was added, and the mixture was set aside at room temperature for eight hours. After removal of solvents under reduced pressure, 0.15 g (71%) of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI), m.p. 126-127°, was obtained.

Demethylation of 3,4,7,8-Tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone. A mixture of 1 g of 3,4,7,8-tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII), 2 g of aluminum chloride, and 10 ml of dry xylene was boiled with stirring for five minutes. After treatment as before, 0.09 g of the above-described 3,4-dihydro-6-p-hydroxyphenyl-1(2H)-naphthalenone (XIV), m.p. 210-212°, was isolated.

Methylation of 6-p-Methoxyphenyl-1-naphthol. A mixture of 0.2 g of 6-p-methoxyphenyl-1-naphthol (XVII) and excess of ethereal diazomethane was allowed to stand for five hours at room temperature. After removal of solvent there remained 0.12 g (57%) of 1-methoxy-6-p-methoxyphenylnaphthalene (XVIII), m.p. 105-106° (from heptane).

Found %: C 81.73; 81.94; H 6.23; 6.37

$C_{18}H_{16}O_2$. Calculated %: C 81.8; H 6.1

Its picrate melted at 95-96° (from alcohol).

Found %: N 8.87; 8.91

$C_{18}H_{16}O_2 \cdot C_6H_3O_7N_3$. Calculated %: N 8.5

Preparation of 1,2-Dihydro-8-methoxy-3-p-methoxyphenylnaphthalene. A solution of 3.6 g of 3,4-dihydro-5-methoxy-2(1H)-naphthalenone (XXI), b.p. 123-125° (1 mm) and n_D^{20} 1.5610 [8], in 15 ml of benzene was added gradually to an ice-cooled stirred Grignard reagent prepared from 0.7 g of magnesium, 6 g of p-bromoanisole, and 20 ml of ether. The solution was refluxed for 90 minutes, allowed to stand for one day at room temperature, and then decomposed with ice and dilute (1 : 1) hydrochloric acid. The ether-benzene layer yielded 2.5 g of an oil, b.p. 200-215° (1 mm), which crystallized out when 80% acetic acid was added. The product was 1.2 g (23%) of 1,2-dihydro-8-methoxy-3-p-methoxyphenylnaphthalene (XIX), m.p. 94-95° (from heptane).

Found %: C 80.99; 80.73 H 6.70; 6.623;
$C_{18}H_{18}O_2$. Calculated %: C 81.2; H 6.8

Dehydrogenation of 1,2-Dihydro-8-methoxy-3-p-methoxyphenylnaphthalene. A mixture of 0.6 g of 1,2-dihydro-8-methoxy-3-p-methoxyphenylnaphthalene (XIX) and 0.2 g of sulfur was heated at 220-225° for 20 minutes. The cooled mass was extracted with a boiling mixture of benzene and heptane in presence of alumina. Filtration and removal of solvents gave 0.4 g (67%) of 1-methoxy-6-p-methoxyphenylnaphthalene (XVIII), m.p. 105-106°, undepressed by admixture of the sample described above.

SUMMARY

1. When the methiodide of 3-dimethylamino-4'-methoxypropiophenone (VIII) or 4'-methoxyacrylophenone (IX) was treated with the sodium derivative of Hagemann's ester (X), a condensation product (XI) was isolated, and boiling of this with aqueous-methanolic caustic potash and subsequent treatment with hydrochloric acid gave a mixture of 3,4,7,8-tetrahydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XII) and 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI). The structures of these compounds were confirmed by a study of their ultraviolet spectra and by independent synthesis.

2. Dehydrogenation of 3,4-dihydro-6-p-methoxyphenyl-1(2H)-naphthalenone (XVI) over palladized charcoal gave 6-p-methoxyphenyl-1-naphthol (XVII), which was converted into 1-methoxy-6-p-methoxyphenylnaphthalene (XVIII) by methylation with diazomethane. This compound was synthesized also by reaction of p-methoxyphenylmagnesium bromide (XXII) with 3,4-dihydro-5-methoxy-2(1H)-naphthalenone (XXI) and dehydration of the alcohol obtained (XX).

3. The tricyclic compounds (XII), (XIII), (XVI), and (XIX) that we have prepared are of interest as steroid analogs in which there is no B ring.

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REDUCTION OF β-AMINO ACIDS WITH LITHIUM ALUMINUM HYDRIDE

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In 1948-49 Karrer and coworkers [1] applied lithium aluminum hydride to the reduction of esters of α-amino acids and showed that the reaction is not accompanied by change in spatial configuration and results in the formation of optically pure β-amino alcohols. In 1952-53 lithium aluminum hydride was applied successfully by Vogl and Pohm [2, 3] to the preparation of β-amino alcohols directly from α-amino acids. When α-amino acids free from other functional groups were treated with a 3-5% solution of $LiAlH_4$ in tetrahydrofuran, the yields of the corresponding β-amino alcohols attained 70-80%.

As we were studying β-amino acids, we also made use of $LiAlH_4$ for their direct reduction to γ-amino alcohols. We carried out this reaction on the following β-amino acids: β-aminohydrochinnamic acid, β-amino-3,4-methylenedioxyhydrocinnamic acid, 3-aminononanoic acid, β-aminocyclohexanepropionic acid, and 3-aminobutyric acid. In this way we obtained the corresponding amino alcohols: 3-amino-3-phenyl-1-propanol, 3-amino-3-(3,4-methylenedioxyphenyl)-1-propanol, 3-amino-1-nonanol, γ-aminocyclohexanepropanol, and 3-amino-1-butanol. It was thus shown that the direct reduction of the carboxy group with lithium aluminum hydride is possible also for β-amino acids.**

EXPERIMENTAL

The reductions with $LiAlH_4$ were carried out both in tetrahydrofuran and in ether; in some cases– e.g. in the case of β-aminohydrochinnamic acid– the yield of amino alcohol was the same in both solvents. The $LiAlH_4$ solution was prepared either from the dry preparation or directly from aluminum chloride and lithium hydride [4, 5]; when it was prepared from aluminum bromide [6], low yields were obtained.

1. Reduction of β-Aminohydrocinnamic Acid. In an atmosphere of nitrogen, 3.3 g of $LiAlH_4$ was added to 66 ml of dry tetrahydrofuran, and the mixture was cooled and stirred while 5.7 g of β-aminohydrocinnamic acid was added gradually. The mixture was heated for three hours in a water bath. On the next day the mixture was diluted with an equal volume of dry ether; it was then cooled strongly, and moist ether was added very cautiously; finally, water was added dropwise. The precipitate that formed was filtered off and boiled several times with alcohol. The alcohol solutions were combined with the main solution, which was dried with potassium carbonate and evaporated under reduced pressure. The oily residue was dissolved in the minimum amount of absolute alcohol, and a large amount of absolute ether was added to the solution. The precipitate that formed was filtered off and washed with absolute ether, and the solution was again evaporated under reduced pressure. The viscous oil that remained rapidly crystallized. The precipitate was filtered off and washed with absolute ether. The product was 3 g of 3-amino-3-phenyl-1-propanol, m.p. 75-76° (needles from benzene). The literature [7] gives m.p. 73°.***

Found %: N 9.15; C 71.42; H 8.88

$C_9H_{13}ON$. Calculated %: N 9.27; C 71.52; H 8.61

The hydrochloride of 3-amino-3-phenyl-1-propanol forms needles of m.p. 125-126° (from absolute alcohol by precipitation with absolute ether).

* Deceased.

** We must mention that, while our investigations were in progress, a paper appeared by Vogl and Pohm [3] in which the reduction of β-alanine to 3-amino-1-propanol by means of lithium aluminum hydride is described.

*** When β-aminohydrocinnamic acid was reduced with $LiAlH_4$ in ether, the yield of 3-amino-3-phenyl-1-propanol was 53-55%. The duration of heating was six hours.

Found %: N 7.69; C 57.83; H 7.67
$C_9H_{14}ONCl$. Calculated %: N 7.47; C 57.60; H 7.47

The picrate of 3-amino-3-phenyl-1-propanol forms yellow needles, m.p. 152-153°.

Found %: N 14.90
$C_{18}H_{19}O_9N_4$. Calculated %: N 14.74

2. Reduction of β-Amino-3,4-methylenedioxyhydrocinnamic Acid. In an atmosphere of nitrogen, 5.1 g of $LiAlH_4$ was added to 95 ml of cooled dry tetrahydrofuran with cooling and stirring, and 10 g of β-amino-3,4-methylenedioxyhydrocinnammic acid was then added slowly. The mixture was heated for six hours in a water bath. On the next day the reaction mixture was treated as in the preceding experiment. The product obtained after removal of solvents was 3.55 g (38%) of 3-amino-3-(3,4-methylenedioxyphenyl)-1-propanol, m.p. 52.5-55° (fine needles from absolute alcohol).

Found %: N 7.39; C 61.36; H 6.62
$C_{10}H_{13}O_3N$. Calculated %: N 7.18; C 61.54; H 6.67

When β-amino-3,4-methylenedioxyhydrocinnamic acid was reduced with $LiAlH_4$ in ether, a poorly crystallizing oil was obtained, and from this, by the action of ethereal hydrogen chloride, the hydrochloride of 3-amino-3-(3,4-methylenedioxyphenyl)-1-propanol, m.p. 176-178°, was obtained.

Found %: N 6.00
$C_{10}H_{14}O_3NCl$. Calculated %: N 6.05

The hydrochloride was reconverted into the base, and from this the picrate, m.p. 184-185°, was prepared.

Found %: N 13.63; C 45.62; H 3.84
$C_{16}H_{14}O_{10}N_4$. Calculated %: N 13.21; C 45.28; H 3.77

3. Reduction of 3-Aminononanoic Acid. In an atmosphere of nitrogen, 7 g of 70% $LiAlH_4$ was added gradually to 100 ml of strongly cooled stirred dry tetrahydrofuran, and 9 g of 3-aminononanoic acid was then added in small portions. The mixture was at first stirred at room temperature, and was then boiled for six hours in a water bath. On the next day the reaction mixture was treated as in Experiment 1. The residue after removal of solvents under reduced pressure was 7.8 g of a yellow oil, which was vacuum-distilled twice. The yield of 3-amino-1-nonanol was 7.0 g (80%), b.p. 120-121° (3 mm).

Found %: N 9.01; C 68.13; H 12.82
$C_9H_{21}ON$. Calculated %: N 8.81; C 67.92; H 13.21

When 3-amino-1-nonanol was allowed to stand in the air, its carbonate was formed, and this could be obtained also by passage of carbon dioxide through an ethereal solution of the amino alcohol; m.p. 89-92°.

Found %: N 7.40
$C_{19}H_{44}O_5N_2$. Calculated %: N 7.37

4. Reduction of β-Aminocyclohexanepropionic Acid. In an atmosphere of nitrogen, 1.5 g of 70% $LiAlH_4$ was added gradually with stirring and cooling to 30 ml of dry tetrahydrofurn, and 1.65 g of β-aminocyclohexanepropionic acid was then added. After six hours the mixture was cooled and treated in the usual way. Solvents were distilled off, and the residue was an oil. Extraction of this oil with a mixture of diethyl ether and petroleum ether gave 0.5 g of the carbonate of γ-aminocyclohexanepropanol, m.p. 127-129°.

Found %: N 7.49
$C_{19}H_{36}O_5N_2$. Calculated %: N 7.45

5. Reduction of 3-Aminobutyric Acid. In an atmosphere of nitrogen, 6.6 g of (70%) $LiAlH_4$ was added gradually with cooling and stirring to 135 ml of absolute ether, and 5 g of 3-aminobutyric acid was then added. The mixture was heated for six hours in a water bath, and then treated in the usual way. The ethereal-alcoholic solution was evaporated under reduced pressure, and the residue was 1.15 g (27%) of 3-amino-1-butanol, b.p. 81-82° (19 mm), which has been described previously [8]. It is probable that the yield could have been improved by carrying out the reaction in tetrahydrofuran. When an attempt was made to determine the melting point of the pure picrate in a block, an explosion occurred; the explosion temperature was 334°.

SUMMARY

Some β-amino acids were reduced to the corresponding amino alcohols with the aid of lithium aluminum hydride.

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SOME REACTIONS OF β-AMINO-1-NAPHTHALENEPROPIONIC ACID AND β-METHYLAMINO-1-NAPHTHALENEPROPIONIC ACID

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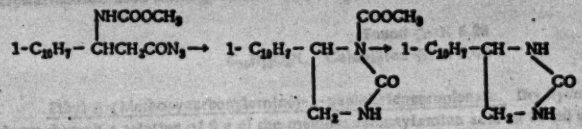
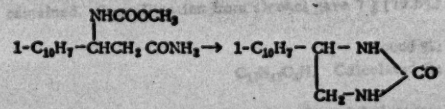
In continuation of our investigations on the chemistry of β-amino-1-naphthalenepropionic acid and its derivatives [1, 2], we have synthesized N-alkoxycarbonyl and N-methyl derivatives of these compounds and studied some of their properties and reactions. We prepared the hydrazides of β-(methoxycarbonylamino)- and β-(ethoxycarbonylamino)-1-naphthalenepropionic acids. The former was submitted to the Curtius reaction, the azide so obtained being heated in dry benzene and converted into 1-(methoxycarbonyl)-5-(1-naphthyl)-2-imidazolidinone [3, 2], which was readily hydrolyzed to 4-(1-naphthyl)-2-imidazolidinone [2]:

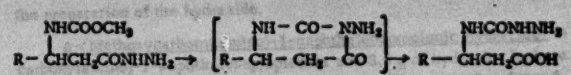


Reaction of β-(methoxycarbonylamino)-1-naphthalenepropionamide with hypobromite at 80° gave the same 4-(1-naphthyl)-2-imidazolidone:



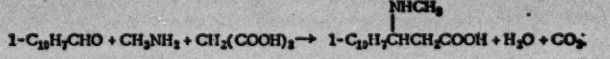
Reaction with hypobromite was therefore accompanied by elimination of the acyl residue.

By the method of Rodionov and Zvorykina [4], the corresponding β-(aminoureido) acid was synthesized from β-(methoxycarbonylamino)-1-naphthalenepropionic hydrazide:



Syntheses of β-methylamino-1-naphthalenepropionic acid was carried out under the following conditions:

1. Heating of 1-naphthaldehyde with malonic acid and methylamine in glacial acetic acid (yield 21.5%):



* Deceased.

2. Under the conditions described by Rodionov and Kurtev for 2-naphthaldehyde [5], namely, heating of 1-naphthaldehyde with malonic acid, methylamine hydrochloride, and anhydrous potassium acetate in glacial acetic acid (yield 37%).

3. From N-(1-naphthylmethylene) methylamine • by heating it with malonic acid:

a) in absolute alcohol (yield 17.2%) under the conditions described by Johnson [6] for the synthesis of β-methylamin.hydrocinnamic acid and by Rodionov and Kurtev [5] for the synthesis of β-methylamino-2-naphthalenepropionic acid;

b) in dry benzene (yield 34.2%) under the conditions used by Rodionov and Yavorskaya [7] for the preparation of β-methylaminohydrocinnamic acid.

In order to characterize β-methylamino-1-naphthalenepropionic acid, its ethyl ester, hydrazide, amide, N-benzoyl derivative, and N-nitroso compound were prepared.

EXPERIMENTAL

β-(Methoxycarbonylamino)-1-naphthalenepropionic Acid. Gradual addition was made of 8.3 ml of methyl chloroformate to a solution of 23.4 g of the hydrochloride of β-amino-1-naphthalenepropionic acid in 208 ml of 10% caustic potash at 2-5° with stirring. Stirring was continued at the same temperature for a further two hours, and the reaction mixture was then acidified with hydrochloric acid. The precipitate that formed was filtered off and washed with water. The product, amounting to 18.8 g (74%), melted at 181.5-183°. Recrystallization from water gave needles of m.p. 182.5-184°.

Found %: N 5.28
$C_{15}H_{15}O_4N$. Calculated %: N 5.05

Ethyl β-(Methoxycarbonylamino)-1-naphthalenepropionate. Dry hydrogen chloride was passed for 4-5 hours through a solution of 9 g of the methoxycarbonylamino acid in 65 ml of absolute alcohol at 60-70°, and the solution was then cooled to 0°, saturated with hydrogen chloride, and set aside overnight. Solvent was removed under reduced pressure, and the residue was treated with water and ether. The ether extract was washed with 5% sodium bicarbonate solution and then with water. When ether was removed, a rapidly solidifying oil remained. Crystallization from alcohol gave 7 g (70.5%) of needles melting at 91.5-93°.

Found %: N 4.68
$C_{17}H_{19}O_4N$. Calculated %: N 4.65

Ethyl β-(Ethoxycarbonylamino)-1-naphthalenepropionate. This was prepared from the ethoxycarbonylamino acid •• under the conditions for the preparation of the ethyl ester of the methoxycarbonylamino acid. The yield of ester, m.p. 43-48°, was 99.7%. It was recrystallized twice from alcohol (needles) and washed with ether; it then melted at 45-51°. The substance of m.p. 45-51° was used without further purification for the preparation of the hydrazide.

β-(Methoxycarbonylamino)-1-naphthalenepropionic Hydrazide. A solution of 7 g of ethyl β-(methoxycarbonylamino)-1-naphthalenepropionate and 3.5 g of hydrazine hydrate in 8 ml of absolute alcohol was boiled over a gauze for 20 minutes. To the thick crystalline mass that formed, 15 ml of absolute alcohol was added and the mixture was heated in a water bath for 1 hour 40 minutes. The precipitate was filtered off and washed with water and alcohol. The yield of hydrazide was 6.29 g (94.2%); m.p. 216-217° (needles from alcohol and plates from water).

• This compound was prepared under the conditions of the synthesis of the corresponding 2-naphthylmethylene compound [5].

•• β-(Ethoxycarbonylamino)-1-naphthalenepropionic acid was prepared by Rodionov and Kravchenko [1].

Found %: N 14.56

$C_{18}H_{17}O_3N_3$. Calculated %: N 14.63

β-(Ethoxycarbonylamino)-1-naphthalenepropionic Hydrazide. This was prepared under the conditions described for the hydrazide of the methoxycarbonylamino acid. Yield 92.9%; m.p. 219-21.1° (needles from alcohol).*

Found %: N 14.39

$C_{16}H_{15}O_2N_3$. Calculated %: N 13.95

β-(Methoxycarbonylamino)-1-naphthalenepropionyl Azide. Concentrated hydrochloric acid (8.25 ml) was added to a boiling suspension of 2 g of the hydrazide in water; the hydrazide dissolved. The solution was filtered and cooled at 0°; it was shaken while a solution of 0.5 g of sodium nitrite in 9 ml of water was added. There was an immediate precipitate, which was filtered off after a few minutes and washed on the filter with ice water. The yield of azide, which melted with decomposition at 41-43°, was 1.95 g (93.7%). When the reaction was carried out in acetic acid solution, the azide was contaminated with simultaneously formed diacylhydrazine, which is insoluble in hot alcohol. After recrystallization from acetic acid it melted at 268-269°.

Found %: N 10.20

$C_{30}H_{30}O_6N_4$. Calculated %: N 10.33

1-(Methoxycarbonyl)-5-(1-naphthyl)-2-imidazolidinone. A solution of 1.94 g of the azide in 50 ml of dry benzene was boiled in a water bath for five hours. Benzene was distilled off, and crystallization of the residue from alcohol gave 0.78 g (44.3%) of a substance of m.p. 191-193° (long rectangular plates).

Found %: N 10.15

$C_{15}H_{14}O_3N_2$. Calculated %: N 10.37

Hydrolysis of 1-(Methoxycarbonyl)-5-(1-naphthyl)-2-imidazolidinone. A suspension of 0.5 g of the (methoxycarbonyl) imidazolidinone in 25 ml of 15% caustic soda solution was boiled for five hours. The precipitate was filtered off and washed with water. Crystallization from alcohol gave 0.27 g (68.9%) of 4-(1-naphthyl)-2-imidazolidinone,** m.p. 220-221°.

β-(Methoxycarbonylamino)-1-naphthalenepropionamide. Sulfuryl choloride (8.72 g) was added to 8 g of the methoxycarbonylamino acid, cooling being applied by means of ice water. The mixture was then heated at 40° for 3-4 hours, and the excess of sulfuryl chloride was distilled off under reduced pressure. The acid chloride was dissolved in dry benzene, and dry ammonia was passed through the solution. The amide was precipitated and was filtered off and washed, first with 2-3% caustic soda solution, then with water, and finally with ether. Two recrystallizations from alcohol gave 5.92 g (74.2%) of amide, m.p. 238-239° (fine flat needles).

Found %: N 10.38

$C_{15}H_{16}O_3N_2$. Calculated %: N 10.29

Reaction of β-(Methoxycarbonylamino)-1-naphthalenepropionamide with Hypobromite. Hypobomite solution was prepared from 29.6 ml of 15% caustic soda solution and 3.5 g of bromine at −7°, and 2.5 g of the amide was added. The mixture was stirred at room temperature, and after 30 minutes the amide had completely dissolved and an oil had separated. After a further 30 minutes the mixture was gradually heated. At 60° the oil became thin, but at 80° it solidified. The mixture was kept for several minutes at 80°. When the mixture was cool, the precipitate was filtered off, washed with water, and recrystallized from alcohol. The

* The ethoxycarbonylamino and methoxycarbonylamino hydrazides are precipitated in the pure state directly from the reaction solutions.

** 4-(1-Naphthyl)-2-imidazolidinone has been prepared previously [2].

product (0.45 g) was found to be identical with 4-(1-naphthyl)-2-imidazolidinone.

β-(3-Aminourcido)-1-naphthalenepropionic Acid. A suspension of 0.6 g of β-(methoxycarbonylamino)-1-naphthalenepropionic hydrazide in 5 ml of 10% caustic potash solution was boiled until the hydrazide dissolved completely (10-15 minutes). The solution was cooled, filtered from a little suspended matter, and acidified with acetic acid. There was a precipitate of 0.43 g (90.4%) of white needles, m.p. 153-154° (from alcohol; clusters of thin plates).

Found %: N 15.41
$C_{14}H_{15}O_3N_3$. Calculated %: N 15.38

Hydrochloride of β-Methylamino-1-naphthalenepropionic Acid. A mixture of 15.6 g of 1-naphthaldehyde, 13 g of malonic acid, 10.1 g of methylamine hydrochloride, 15 g of anhydrous potassium acetate, and 50 ml of glacial acetic acid was heated in a water bath for nine hours; at the beginning of the heating the mixture frothed strongly. A thick crystalline mass was formed, and 60 ml of 7-8% hydrochloric acid was stirred in. The mixture was heated at 70-80° for ten minutes. The crystals present were filtered off, washed two or three times with 7-8% hydrochloric acid at 70-80°, and then washed with water. The yield of the 1-naphthaleneacrylic acid so obtained was 9.7 g (49%). The acid solution was evaporated down to 200-250 ml, and then cooled. The crystals of the hydrochloride of the amino acid which then came down were filtered off, dried, and washed with ether; yield 9.8 g (37%); m.p. 198.5-200° (long rectangular plates from absolute alcohol).

Found %: N 5.16
$C_{14}H_{16}O_2NCl$. Calculated %: N 5.27

β-Methylamino-1-naphthalenepropionic Acid. This was prepared by treating a thick suspension of its hydrochloride with saturated sodium acetate solution. The hydrochloride dissolved completely, and then a precipitate of the amino acid formed. It crystallized from alcohol in needles, m.p. 191-192°.

Found %: C 73.29; H 6.62; N 5.83
$C_{14}H_{15}O_2N$. Calculated %: C 73.31; H 6.60; N 6.11

Ethyl β-Methylamino-1-naphthalenepropionate. Absolute alcohol (50 ml) was added to 6 g of the hydrochloride of the methylamino acid, and dry hydrogen chloride was passed at 60-70° for 4-6 hours. The hydrochloride of the amino acid slowly dissolved, and another crystalline substance was simultaneously precipitated. The mixture was cooled, the precipitate was filtered off, and excess of solvent was distilled from the reaction solution under reduced pressure. The residue crystallized and was purified together with the crystals that appeared earlier by recrystallization from small amounts of absolute alcohol. After being washed with dry ether, the crystals melted at 145.5-146.5° (long hexagonal plates). The yield of ester was 5.51 g (about 83%).

Found %: N 4.67
$C_{18}H_{20}O_2NCl$. Calculated %: N 4.77

β-(N-Methylbenzamido)-1-naphthalenepropionic Acid. Benzoyl chloride (10.5 ml) was added at 20° over ten minutes to a stirred solution of 2 g of the hydrochloride of the methylamino acid in 17 ml of 10% caustic potash. The mixture was then kept at the same temperature for two hours. The precipitate obtained by acidification with hydrochloric acid was filtered off and carefully washed with boiling water; yield 2.15 g (85.7%); m.p. 173-174°. After recrystallization from alcohol the melting point was 175-177° (long octagonal prisms).

Found %: N 4.39
$C_{21}H_{19}O_3N$. Calculated %: N 4.20

β-(Methylnitrosamino)-1-naphthalenepropionic Acid. A solution of 0.34 g of sodium nitrite in 3.4 ml of water was added at 26° to a mixture of 1 g of the hydrochloride of the methylamino acid and 6.75 ml of 3% hydrochloric acid. The precipitate immediately dissolved, and a yellow viscous oily layer formed on the surface. After 30 minutes the mixture was heated to 35° and set aside overnight. The oily layer solidified. The yield of the nitroso compound, m.p. 125-128°, was 0.75 g (77.2%). When attempts were made to crystallize it from alcohol or aqueous alcohol, an emulsion was formed from which the product crystallized out after 1-2 days; m.p. 124-126° (prisms).

Found %: N 11.00
$C_{14}H_{14}O_3N_2$. Calculated %: N 10.85

β-Methylamino-1-naphthalenepropionic Hydrazide. The free base was liberated from 3.46 g of the hydrochloride of the ethyl ester of the methylamino acid by the action of 20% sodium carbonate solution. The product was extracted with ether from the emulsion then obtained, ether was removed, and the residue was dried in a desiccator. The oily free base and 1.73 ml of hydrazine hydrate were dissolved in 4.5 ml of absolute alcohol, and the solution was boiled for 5-6 hours. Alcohol and excess of hydrazine hydrate were distilled off under reduced pressure, and the residue was washed with ether and water. The product (2.6 g) was recrystallized from water or aqueous alcohol (needles), and after being dried at 80° and 10 mm for three hours it melted sharply at 113-114°.

Found %: N 17.63
$C_{14}H_{17}ON_3$. Calculated %: N 17.28

β-Methylamino-1-naphthalenepropionamide. The free base was liberated from 1.5 g of the hydrochloride of the ethyl ester of the methylamino acid (see preceding experiment) and was dissolved in 18 ml of absolute alcohol. The solution was saturated with dry ammonia. After three weeks the alcohol was distilled off, and the oil that remained was treated with ether. There was a precipitate, which was filtered off, washed with water and with ether, and recrystallized from water. Long hexagonal plates were obtained; m.p. 130-132°; yield 0.412 g (35.4%).

Found %: N 12.08
$C_{14}H_{15}ON_3$. Calculated %: N 12.28

SUMMARY

1. β-Methylamino-1-naphthalenepropionic acid and some of its derivatives were prepared.

2. The previously described β-amino-1-naphthalenepropionic acid was converted into 4-(1-naphthyl)-2-imidazolidinone by Hofmann's reaction—treatment of β-(methoxycarbonylamino)-1-naphthalenepropionamide with hypobromite—and by the Curtius reaction—heating of β-(methoxycarbonylamino)-1-naphthalenepropionyl azide in benzene. The primary product in the latter case was 1-(methoxycarbonyl)-5-(1-naphthyl)-2-imidazolidinone, which was obtained in high yield, and this was readily hydrolyzed to 4-(1-naphthyl)-2-imidazolidinone.

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CHLORINATION OF ALKANES IN PRESENCE OF NITROGEN DIOXIDE

V. A. Nekrasova and N. I. Shuikin

In our previous investigations [1] the chlorination of alkanes was carried out at a molar ratio of hydrocarbon to chlorine of 10 : 1. Excess of hydrocarbon was found to be essential for the avoidance of explosions, which can occur under the conditions of vapor-phase chlorination. In order to utilize the unchanged hydrocarbons more fully, after separation from the chloro derivatives they were again chlorinated, a procedure that complicated the preparation of haloalkanes. In these investigations 1% of unsaturated hydrocarbons was added to the hydrocarbon as a chain initiator.

In the present investigation we carried out the chlorination of alkanes in presence of nitrogen dioxide (2%). The presence of this homogeneous catalyst was favorable to uniform reaction without explosions and enabled us to carry out vapor- and liquid-phase chlorination of C_6–C_{12} n-alkanes at a molar ratio of hydrocarbon to chlorine of 1 : 1 and a rate of passage of chlorine into the reaction zone of 1.2 liters per hour.

For the vapor-phase chlorination of hexane and heptane, comparatively high temperatures, 265-320°, were necessary; in the liquid phase the chlorination of these hydrocarbons was extremely slow. The optimum temperature for the chlorination of C_8–C_{12} alkanes rises only slightly with increase in molecular weight, and for these hydrocarbons both vapor-phase and liquid-phase chlorination are possible. The vapor-phase chlorination of dodecane and higher hydrocarbons is difficult, for a high temperatures the chloro compounds formed are partially decomposed with separation of carbon and formation of gases.

EXPERIMENTAL

Our raw material for the preparation of chloro derivatives of alkanes was a straight-run gasoline derived from Crimean petroleum. The normal hydrocarbons were separated from isomers and cyclic hydrocarbons by means of the urea complex [2]. They were then subjected to precise rectification through a 70-plate column. The hydrocarbons isolated had the properties shown in Table 1.

Undecane and dodecane were separated from the ligroin fraction of Crimean petroleum via the urea complexes; they had the following properties—undecane: b.p. 195-196° (757 mm), d_4^{20} 0.7403, and n_D^{20} 1.4172 dodecane: b.p. 215.5-217° (755 mm), d_4^{20} 0.7489 and n_D^{20} 1.4218.

The vapor-phase thermal chlorination of C_6–C_{12} alkanes was carried out in the apparatus described in a previous paper [3]. For the rather volatile hydrocarbons (C_6 and C_7), the lengths of the tubes of the coil reactor may be increased to two or more meters.

By the way of example we shall describe briefly the results of the separation of the products of the vapor-phase chlorination of dodecane. The chlorination of 85 g of dodecane was carried out at 400° at the molar ratio of hydrocarbon to chlorine and the rate of introduction of chlorine indicated above. Fractionation of the chlorination product (83 g) gave the following fractions:

Fraction I, b.p. 243–245° (578 mm); 37.0 g (44.6%); n_D^{20} 1.4380; d_4^{20} 0.8614; Cl 17.29%

Fraction II, b.p. 255–257° (758 mm); 23.7 g (28.5%); n_D^{20} 1.4425; d_4^{20} 0.8670; Cl 17.28%; Found MR 62.47; Calculated for $C_{12}H_{25}Cl$ MR 62.48

Fraction III, b.p. 257–259°; 17.4 g (21%)

Residue 4.9 g (5.9%).

On the basis of a comparison of its constants with data in the literature [4], Fraction 1 was taken to be secondary monochloro compounds. Fraction 2 corresponded to 1-chlorodecane, and Fraction 3 to mixture of dichloro derivatives. The results of experiments carried out under optimum conditions are given in Table 2.

TABLE 1

Properties of n-Alkanes Isolated from Crimean Gasoline

Hydrocarbon	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
Hexane	68—69 (751)	1.3750	0.6594
Heptane	98—99 (754)	1.3878	0.6838
Octane	125—126 (754)	1.3975	0.7026
Nonane	150—151 (751)	1.4054	0.7177
Decane	174—175 (750)	1.4120	0.7298

It follows from Table 2 that under the given conditions, the highest yields of primary chloro compounds are obtained in the chlorination of octane, nonane, and decane when the temperature is in the range 365-385°. The chloro compounds obtained were washed with sodium carbonate solution and with water, dried with anhydrous calcium chloride, and subjected to precise rectification. The properties of the monochloro derivatives are given in Table 3.

The values obtained for the constants of the primary monochloro compounds are in accord with data in the literature [4].

The liquid-phase chlorination of C_5-C_{12} alkanes was also carried out. It was found that hexane at 66° and heptane at 95° are chlorinated with formation of 67-71% of chloro derivatives, mainly monochloro compounds. The chlorination results are given in Table 4.

TABLE 2

Vapor-Phase Chlorination of Alkanes in Presence of Nitrogen Dioxide

Original alkane	Chlorination temperature °C	Yield of chloro derivative (% on the hydrocarbon that reacted)			
		Primary monochloro	Secondary monochloro	Dichloro	Residue and losses
Hexane	285	50.0	15.6	28.6	5.8
Heptane	320	50.5	16.0	29.0	4.5
Octane	365	60.5	23.5	14.0	2.0
Nonane	380	59.0	22.8	16.0	2.2
Decane	385	57.0	23.0	18.2	1.8
Undecane	390	49.0	30.0	19.0	2.0
Dodecane	400	28.5	44.6	21.0	5.9

TABLE 3

Physicochemical Properties of the Primary Monochloro Compounds Isolated

Chloroalkane from alkane	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR		Chlorine content (%)	
				found	calc.	found	calc.
1-Chloro-hexane	135—137 (758)	0.8760	1.4236	35.0	35.04	29.20	29.19
1-Chloro-heptane	159—161 (756)	0.8726	1.4284	39.36	39.4	26.40	26.37
1-Chloro-octane	183—185 (757)	0.8920	1.4425	43.88	44.01	23.90	23.88
1-Chloro-nonane	202—204 (755)	0.8806	1.4402	48.68	48.63	21.84	21.82
1-Chloro-decane	222—224 (754)	0.8697	1.4380	53.29	53.25	20.12	20.09
1-Chloro-undecane	240—242 (754)	0.8677	1.4399	57.89	57.86	18.63	18.61
1-Chloro-dodecane	255—257 (758)	0.8670	1.4425	62.47	62.48	17.26	17.25

TABLE 4

Liquid-Phase Chlorination of Alkanes in Presence of Nitrogen Dioxide

Original alkane	Chlorination temperature (°C)	Yield of chloro derivative (% on the hydrocarbon that reacted)			
		Primary monochloro	Secondary monochloro	Dichloro	Residue and losses
Octane	123	18.3	61.8	17.6	2.3
Nonane	148	21.2	51.4	24.7	2.7
Decane	172	19.7	53.4	24.3	2.6
Undecane	193	15.0	58.5	23.7	2.8
Dodecane	213	14.3	60.0	22.5	3.2

A comparison of Tables 2 and 4 shows that liquid-phase chlorination results in the formation mainly of secondary chloro compounds, whereas chlorination in the vapor phase gives mainly primary monochloro compounds. The process of introducing chlorine atoms formed by the thermal dissociation of Cl_2 [5] into the molecule of a saturated hydrocarbon is a chain reaction, and the presence of a small amount (2%) of nitrogen dioxide facilitates the formation of the free radical [3].

SUMMARY

1. A study was made of the reaction of chlorine with C_6–C_{12} n-alkanes in presence of nitrogen dioxide in the vapor and liquid phases.

2. Optimum conditions for the synthesis of primary and secondary chloro compounds were found.

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RELATIVE ACTIVITIES OF NICKEL, ZINC, AND CHROMIUM OXIDES, SULFIDES, AND SELENIDES IN THE CATALYTIC DECOMPOSITION OF ISOPROPYL ALCOHOL

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It is known that in some catalytic organic reactions nickel sulfide exhibits very satisfactory activity and high selectivity. There are many patents relating to this catalyst, and there are also some papers on its properties and field of application. The most important of these papers have been treated in a general review [1]. Selenides and tellurides have received very little study, being considerably less accessible than sulfides. From the point of view of the principle of structural correspondence developed in the multiplet theory of catalysis, it was of interest to obtain data characterizing the comparative activities of oxides, sulfides, selenides, and tellurides of nickel and some other metals under the same conditions in the same reactions, and to investigate their structural properties and phase composition. This was the object of the present investigation, and we selected nickel, zinc, nickel-zinc, and chromium catalysts for study. Unfortunately, we did not succeed in preparing the tellurides of these metals in a form suitable for catalysis. We prepared the catalysts and studied their activities in the following reactions: 1) decomposition of isopropyl alcohol; 2) selective hydrogenation of 1,3-butadiene to butene; and 3) reduction of nitrobenzene to aniline. In this paper we give the results of the work with isopropyl alcohol, and the next paper is devoted to a description of the other two reactions.

The group of catalysts selected for investigation are of interest also in connection with the allotropy (polymorphism) of some of the compounds present. The importance of investigating such substances and their phase transformations was pointed out by one of us in a review article, in which the question of the structural correspondence between reactant and catalyst was examined [2].

EXPERIMENTAL

The methods of preparing oxide and many sulfide catalysts are given in fair detail in the literature. For the preparation of selenides and tellurides the following methods can be used: Method A- The preparation of, for example, NiSe [3] and ZnTe [4] by direct combination of the elements at high temperature in an inert atmosphere. These reactions are highly exothermic, and considerable sintering with formation of a coarsely dispersed system is therefore inevitable. It follows that such a method for preparing a catalyst is unsuitable, and in fact the zinc telluride that we prepared in this way was quite inactive. Method B- Reduction of salts of the appropriate acids, e.g. $ZnSeO_3$, $NiSeO_3$, etc. [5], obtained by double decomposition with the sodium salts (Na_2SeO_3). Method C- Action of hydrogen selenide or telluride or its sodium salt on a salt of the appropriate metal (in particular ZnSe [6, 7], $NiTe_2$ [8], and chromium selenide [9] have been prepared in this way). Methods B and C have similar defects: a great tendency for contamination with compounds contained in the mother liquor, and the danger that the desired compounds will be hydrolyzed during the washing of the precipitates. Method D is the most convenient—the direct action of hydrogen selenide or telluride on the oxide or hydroxide of the appropriate metal. In this method the only volatile reaction product—the water formed—is readily removed from the reaction zone by the gas that is passing (H_2Se+N_2), and hydrolysis products, if formed, will again enter the reaction. This method, which has been described in detail for the preparation of nickel sulfide [1] and which permits the use of ready prepared oxide catalysts and of hydroxides (washed completely free from soluble salts), was the one that we used in the present work. For our purpose, this method had the further advantage that there was a genetic relationship in each series of O-, S-, and Se-catalysts and differences in content of impurities were kept to a minimum.

* Deceased.

NiO, ZnO, Cr_2O_3, and NiO-ZnO (25 mole-% NiO) were prepared from 10% solutions of the nitrates, which were precipitated at 65° with 10% solutions of KOH (Ni, Zn) and NH_3 (Cr_2O_3 and Ni-Zn). The hydroxides were washed until free from nitrate ions (diphenylamine as indicator), and were then formed into shape and dried at 120°. Part of each hydroxide was calcined in the air at 450° for seven hours, and part was set aside for conversion into sulfide and selenide.

The sulfide catalysts were prepared from the hydroxides (formed and dried at 120°) by passing hydrogen sulfide directly into the catalysis tube at 110-120° in the case of the nickel and mixed nickel-zinc catalysts and at 120-140° in the case of the zinc and chromium catalysts. Passage of a mixture of hydrogen sulfide and nitrogen was continued for some time after reaction was complete in order to facilitate the removal of water vapor, and the catalysts were cooled in this atmosphere. The catalysts did not smell of hydrogen sulfide. The preliminary heating of these, and also of the selenide catalysts, was carried out at the temperature of the experiment, and not at 450°, as in the case of the oxides.

The selenide catalysts were prepared similarly. Hydrogen selenide was prepared by passing electrolytic hydrogen, freed from oxygen, through molten selenium at 400° (in a quartz test tube). The gas passed over the hydroxide was therefore a mixture of hydrogen selenide and hydrogen. In other respects, the preparation of the catalysts was similar to that of the sulfides.

The specific surfaces of the catalysts were determined both before and after each series of experiments with the given catalyst. The determinations were based on adsorption isotherms for benzene vapor at 20°, which were measured in an apparatus incorporating a quartz spring balance, the surfaces of the samples being first cleaned by exposure at 200-300° to a high vacuum until constant weight was attained. The results are given in Table 1 together with X-ray phase analysis data, which were obtained with series-K_α chromium radiation, a vanadium filter being used for the removal of β-radiation.

The phase analysis was carried out by comparing the values found for the interplanar spacings and the intensities of the corresponding lines with the values for the pure substances (possible components of the catalysts) given in the literature. For NiO, $Ni(OH)_2$, ZnO, α- and β-ZnS, and Cr_2O_3, use was made of tabular data on standard X-ray diagrams [10]. For the remaining compounds the data were taken from their original sources: NiS [11-13], Ni_3S_2 [14], NiSe [13, 15-17], ZnSe [18], CrS and CrSe [15]. As will be seen from Table 1, in some cases the phase composition of the catalyst had changed after the experiment; moreover, some of the catalysts, even in their original state, were polyphase systems.

The experiments were carried out with isopropyl alcohol (fraction 81.5-82°) that had been rendered absolute by treatment first with calcium oxide, and then with metallic calcium. Of the two possible ways in which it could decompose, dehydrogenation was followed by measuring the volume of hydrogen formed, and dehydration by measuring the volume of propene (STP). The conditions in the preparatory stage of the experiment—the time required to raise the temperature to the required value, the time required to check the constancy of this temperature, the amount of decomposition products of isopropyl alcohol required to remove foreign gas from the system—were kept standard in all cases. The experiments were carried out in the usual continuous catalysis system, the temperature being measured by the aid of a thermocouple placed at the center of the catalyst layer. Liquid reaction products and unchanged alcohol were separated in a receiver fitted with reflux condenser, and gaseous products were collected above saturated brine in a constant-level receiver and were analyzed for carbon dioxide, carbon monoxide, propene, hydrogen, and saturated hydrocarbons. As carbon monoxide was formed only in a few experiments and only in very small amounts (not more than 1.3 ml per milliliter of alcohol passed), we have not included the relevant data in Table 2.

In all experiments the volume of catalyst was 10 ml and its grain size was 1.5 x 3 mm; isopropyl alcohol was passed at a space velocity of 0.6×0.02 hour^{-1}. The experimental results are given in Table 2 in the form: a) of degrees of conversion, characterized by the volumes (STP) of the components of the gas mixture formed from 1 ml of alcohol *, and b) of specific activities—the volumes (ml) of hydrogen and propene formed in the passage of 1 ml of alcohol over 1 g of catalyst. The variation of catalyst activity with temperature is shown in Figures 1-4. During each individual experiment the rate of decomposition of the alcohol was constant. As stated above, some catalysts changed in composition during the experiments: this was shown by

* As the volume of catalyst was 10 ml, the specific activities per unit volume were 0.1 of these values.

TABLE 1

Physical Properties of Catalysts and their Compositions According to the Results of X-Ray Phase Analysis

No.	Catalyst	Bulk density (g/cc)	Specific surface (sq. m/g)		Composition according to X-ray Phase Analysis	
			Original	After experiments	Original catalyst	Catalyst after decomposition experiments
1	NiO	0.75	24	38	NiO	NiO, $Ni(OH)_2$, Ni
2	NiS	0.90	6.4	—	β-NiS, γ-NiS	β-NiS, Ni_3S_2
3	NiSe	2.05	27	21	NiSe, NiO?	NiSe, NiO, $Ni(OH)_2$?
4	ZnO	0.50	38	—	ZnO	ZnO
5	ZnS	0.55	17	19	α-ZnS, β-ZnS, ZnO	α-ZnS, β-ZnS, ZnO
6	ZnSe	0.85	1.4	14	ZnSe	ZnSe, ZnO
7	Cr_2O_3	0.80	24	—	Cr_2O_3	Cr_2O_3
8	CrS	0.70	190	83	Amorphous to X-rays	Amorphous to X-rays
9	CrSe	1.1	38	—	"	"
10	NiO — ZnO .	0.20	11	14	NiO, ZnO	NiO, ZnO
11	NiS — ZnS . .	0.22	15	43	Amorphous to X-rays	α-ZnS, β-ZnS, β-NiS
12	NiSe — ZnSe .	0.35	21	13	NiSe, Ni_3Se_2,? ZnSe, ZnO	NiSe, NiO, ZnSe, ZnO, Ni_3Se_2?

• A question mark indicates that the presence of the phase has not been established with certainty.

phase-composition determinations after each series of experiments with a particular catalyst. Owing to this change in composition, in experiments with NiSe—even at 245°—the end of the catalysis tube and the walls of the receiver were very quickly covered with a red deposit of elementary selenium. A similar phenomenon was observed also for ZnSe. When sulfide catalysts were used, the water in the receiver for gaseous products gradually became turbid (opalescent) owing to the appearance of elementary sulfur. These visible changes were in accord with the results of phase analysis (Table 1).

Discussion of Experimental Results

It may be expected that the following phases may be present in the catalysts investigated: hexagonal ZnO (wurtzite type: a = 3.22 A; c = 5.16 A; c/a = 1.61) and α-ZnS (wurtzite: a = 3.84 A; c = 6.28 A; c/a = 1.64); face-centered cubic β-ZnS (sphalerite: a = 5.34 A), ZnSe (a= 5.66 A), and NiO (a= 4.17 A); amorphous α-NiS, hexagonal β-NiS (a = 3.24; A; c = 5.30 A, c/a = 1.55), being the most stable form of nickel sulfide, and rhombohedral γ-NiS (a = 9.61 A; c = 3.45; c/a = 0.32). Nickel sulfides undergo the phase transformations $\alpha \rightarrow \gamma \rightarrow \alpha\beta$, which occur spontaneously at moderate temperatures. There is the further possibility of the presence in the catalysts of nickel subsulfide Ni_3S_2, the rhombohedral lattice of which differs very little from a cubic lattice a = 4.04 A; α = 90.3°). There are also the nickel selenides [13], which are isomorphous with the sulfides: γ-NiSe (a = 9.84 A; c = 3.18 A; c/a = 0.32) and β-NiSe (a = 3.66 A; c = 5.33 A; c/a = 1.46). Possible chromium compounds are the rhombohedral oxide (a = 5.35 A; α= 54°58'), the hexagonal sulfide (a = 3.44 A; c = 5.67 A; c/a = 1.65), and the selenide (a = 3.59 A; c = 5.80 A; c/a = 1.62). The formation of hydroxides cannot be excluded, and in the case of nickel catalysts reduction to the metal may occur. As will be seen from Table 1, many of the catalysts are polyphase systems even before the experiments. We will indicate the most important cases of changes in phase composition occurring during the experiments with the catalysts. We must first point out the appearance of crystalline phases in the originally amorphous catalyst No. 11 (Table 1), which can be explained by the reorientation of particles at the temperature of the experiments; the increase in the surface area of this catalyst must be attributed to the formation of new phases, ZnO and NiO, during the experiments. Again, in the nickel sulfide catalyst No. 2, the γ-NiS phase disappeared during the experiments owing to transformation into β-NiS, and the subsulfide Ni_3S_2 made its appearance; as will be seen from Fig. 1, these changes in phase composition were accompanied by change of activity in the alcohol-decomposition reaction.

TABLE 2

Experimental Results

Catalyst	Temperature (°C)	Amount of gas formed from 1 ml of alcohol (STP)					Specific Activity
		In all	CO_2	C_nH_n	H_2	Saturated hydrocarbons	
NiO	245	207.6	5.8	—	189	12.9	25.2
	295	240.7	13.7	1.7	136.8	87.1	18.5
	340	270.2	20.0	7.3	174.2	67.9	24.2
NiS	245	65.8	0.7	64.4	—	0.7	7.2
	295	271.4	3.0	252.3	4.6	11.2	28.6
	340	196.0	1.2	187.8	2.9	3.7	21.2
NiSe	245	No reaction occurred					
	295	31.8	0.2	9.1	19.8	2.8	1.4
	340	40.0	0.3	3.7	33.6	2.0	1.7
ZnO	245	No reaction occurred					
	295	128.1	0.4	3.7	120.5	3.5	24.8
	340	260.9	0.5	13.8	244.0	2.6	53.8
ZnS	245	No reaction occurred					
	295	124.1	—	89.2	33.4	1.5	22.4
	340	315.9	1.2	229.0	81.3	3.8	57.0
ZnSe	245	No reaction occurred					
	295	224.8	—	12.4	212.4	—	28.4
	340	299.3	1.2	19.8	278.3	—	35.2
Cr_2O_3	245	No reaction occurred					
	295	103.1	1.2	37.0	63.1	1.5	12.5
	340	208.5	0.2	104.3	102.7	1.2	26.0
CrS	245	25.7	0.5	14.0	8.4	2.7	3.2
	295	151.3	9.6	78.9	49.3	13.0	18.4
	340	247.1	8.4	162.4	56.1	20.0	31.2
CrSe	245	98.5	—	96.0	2.5	—	9.0
	295	228.2	—	214.5	6.8	6.8	20.0
	340	260.7	0.8	230.4	14.9	14.6	22.3
NiO — ZnO	245	56.7	0.6	—	55.7	0.4	27.8
	295	244.0	0.7	—	241.3	2.0	120.6
	340	261.6	2.1	5.8	247.4	5.0	128.6
NiS — ZnS	245	34.0	0.2	33.4	—	0.4	15.2
	295	276.4	1.4	271.2	—	2.8	123.0
	340	188.9	1.7	172.5	10.5	4.3	83.4
NiSe — ZnSe	245	No reaction occurred					
	295	76.8	1.2	73.0	1.1	1.1	21.2
	340	82.5	0.2	80.7	0.8	0.9	23.3

In a number of cases (catalysts No. 2, 9, 12) oxides were detected in the catalysts after the experiments, these being probably formed by the hydrolysis of sulfides and selenides. Some metallic nickel was found in catalyst No. 1 after the whole series of experiments had been carried out over it. It must be emphasized that in these cases the phase transformations occurred throughout the mass, since the compounds concerned were detected by X-ray structure analysis. In view of this, it may be assumed that similar chemical changes in the catalysts occurred also in other cases, but were localized on the surface, the concentrations of the new phases being insignificant.

Phase analysis showed, therefore, that the investigated sulfide and selenide catalysts are systems of low stability, which undergo appreciable change under the conditions of the alcohol-decomposition reaction. Table 1 shows also that catalysts No. 2, 3, 6, 7, 8, and 9 had high bulk densities. In the original state, catalysts No. 2 and 6 had very low specific surfaces. Sintering during use was greatest for catalyst No. 8, the specific surface of which fell from 190 to 83 sq. m/g. The specific surface of NiO increased during the experiments, owing, apparently, to the appearance of the new phase $Ni(OH)_2$; the same occurred with ZnSe, owing to partial formation of ZnO, and with NiS-ZnS, for which the phase composition in the original catalyst is unknown, since it was amorphous to X-rays. In the remaining cases the change in specific surface during the experiments was insignificant.

Figures 1-4 represent the variation of overall specific activity with temperature (cf. Table 2; the separate specific activities for the two reactions can be readily determined from these data and the data in Table 3). In our experiments the specific activity diminished in the series O > S > Se, in spite of the fact that NiS had a lower specific surface than the oxide and selenide, the specific surfaces of which were almost the same. At 245° the zinc catalysts were inactive, at 295° their activities were in accordance with the series Se > O ≈ S, and at 340° the series was S > O > Se, the selenide having a negligibly low specific surface. Incidently, our crystalline zinc sulfide catalyst differed in activity and phase composition from the similar catalyst prepared by the wet method [19]; in particular, it differed in phase composition after the experiments. For the chromium catalysts the activity series was Se > S > O at 245° and 195°, changing at 345° to Se > S ≈ O; it must be mentioned that the specific surface of the selenide was 50% higher than that of the oxide. The mixed Ni-Zn catalysts gave the same activity series as the nickel catalysts (O > S > Se), from which it follows that the properties of these catalysts are determined more by the nickel compounds than by the zinc compounds.

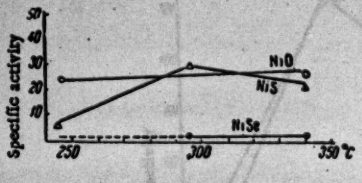

Fig. 1

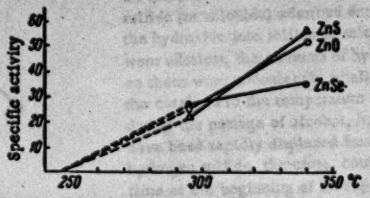

Fig. 2

As a second characteristic of the catalysts, in Table 3 we give selectivity coefficients, $\frac{H_2}{H_2 + C_2H_6}$, i.e. the contribution made by dehydrogenation in the overall reaction. It will be seen that, whereas the mixed oxide catalyst No. 10 was exclusively dehydrogenating, the sulfide and selenide catalysts No. 11 and 12 were exclusively dehydrating. Similarly, nickel sulfide differed greatly in selectivity from the oxide and selenide: the last two catalysts were mainly dehydrogenating, and the sulfide was almost entirely dehydrating. There was an almost equally sharp difference between zinc selenide and oxide, on the one hand, and the sulfide, on the other. It is difficult to imagine that this difference in the sulfides was the result of the replacement of O in corresponding compounds by S or Se, for all these nonmetals belong to the same group of the periodic system and form compounds having similar chemical properties with the metals investigated—in some cases they even form isomorphous compounds. The great difference in selectivity in the cases described must rather be attributed to the liberation of hydrogen sulfide during the changes in phase composition of the catalysts (formation of Ni_3S_2 from NiS and ZnO from ZnS; see Table 1, phase composition after experiments). The hydrogen sulfide evolved is apparently in an active state and—being an acid, i.e. a catalyst for dehydration by the ionic mechanism—changes the ratio of the rates of the simultaneous reactions in favor of dehydration (the effect of adsorbed acids on selectivity is described in the paper [20]. A similar explanation serves for the selectivity of NiS-ZnS and NiSe-ZnSe. For the chromium catalysts, however, such an explanation is inadequate, for it is not confirmed by the change in phase composition, which could not be determined owing to the amorphous structures of the selenide and sulfide during the experiments, and, moreover, the selectivity coefficient varies regularly throughout the series, diminishing in the order O > S > Se at all experimental temperatures. Also, there is a great difference between the selectivities

TABLE 3

Selectivity Coefficients of Catalysts

Temperature	Ni			Zn			Ni – Zn			Cr		
	O	S	Se	O	S	Se	O	S	Se	O	S	Se
245	1	0.02	—	—	—	—	1.0	0	—	—	0.38	0.03
295	0.99	0.015	0.69	0.97	0.27	0.95	1.0	0	0.02	0.63	0.38	0.03
340	0.96	0.006	0.00	0.95	0.26	0.93	0.98	0	0.01	0.50	0.26	0.06

of sulfide and selenide, the selenide being more dehydrating than the sulfide, which was not observed in the cases described above. We consider that the observed differences in the selectivities of chromium catalysts, and also to some extent in the other catalysts discussed above, are associated with differences in the interatomic distances in the lattices of the O, S and Se compounds and with the distribution of alcohol molecules on these lattices—i.e. with the structural factor. We will return to this question in our next paper, which is devoted to hydrogenation reactions on the same catalysts.

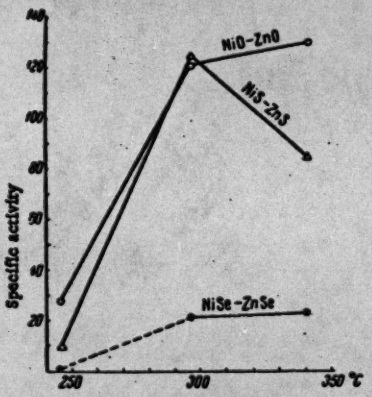

Fig. 3

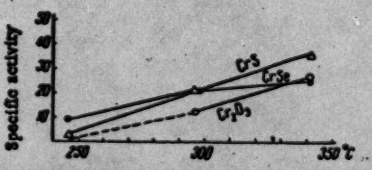

Fig. 4

In discussing the causes of the variation in the selectivity of sulfides, and in some cases also selenides, we must take account of the possible effect of hydrogen sulfide (or selenide) adsorbed during the conversion of the hydroxide into sulfide or selenide. As the catalysts were odorless, the amounts of hydrogen sulfide adsorbed on them were undoubtedly small. During the heating of the catalysts to the temperature of the experiments and during the passage of alcohol, hydrogen sulfide must have been rapidly displaced from the surface. Adsorbed hydrogen sulfide, therefore, could act for only a short time at the beginning of an experiment, and not through the whole series. On the other hand, hydrogen sulfide formed in the above-described phase transformations is evolved over a long period. It is for this reason that we consider that, in the cases discussed above, processes associated with change in phase composition form the basis of one of the main causes of change in selectivity.

In conclusion, we will compare activities in each group—oxides, sulfides, and selenides—of the catalysts investigated. At 245° and 295° the most active oxide catalysts are NiO-ZnO and NiO, and at 340° decomposition of the alcohol occurs at about the same rate over all of the oxides investigated. At 245° all of the sulfides are of low activity, and ZnS is completely inactive; rise in temperature to 295° results in a great rise in activity, which is in the order NiS—ZnS > NiS > Cr_2S_3 > ZnS; and further rise in temperature to 340° causes the activities of the last two to be increased and those of the first two to be diminished. Of the selenides investigated, the most active were those of chromium and zinc; the mixed catalyst was of lower activity, and the activity of nickel selenide was very low.

SUMMARY

1. Data were obtained on the activites of oxides, sulfides, and selenides of nickel, zinc, and chromium and of the corresponding mixed Ni-Zn catalysts in the decomposition reaction of absolute isopropyl alcohol.

The changes in the phase compositions of these catalysts were determined, and their specific surfaces were measured under the conditions of the experiments.

2. It was shown that, under the conditions of the alcohol-decomposition reaction, sulfide and selenide and selenide catalysts are unstable systems. Thus, NiS undergoes a phase transformation into Ni_3S_2 with evolution of hydrogen sulfide, and ZnS undergoes a phase transformation into ZnO (hydrolysis).

3. It was found that the evolution of hydrogen sulfide or selenide which accompanies the phase transformations results in a great change in the selectivity of the catalysts (instead of dehydrogenating, they become dehydrating). Also, the variation in selectivity among metal oxides, sulfides, and selenides depends also on the interatomic distances in the crystal lattices of these substances, this being particularly evident in the chromium catalysts.

4. With respect to their activities in the decomposition of absolute isopropyl alcohol, metal oxides, sulfides, and selenides may be arranged in the following series: NiO > NiS > NiSe; ZnS > ZnO > ZnSe (340); CrS > CrSe > Cr_2O_3. The mixed Ni-Zn catalysts form the same activity series as the nickel catalysts.

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ACTIVITIES OF NICKEL, ZINC, AND CHROMIUM OXIDES, SULFIDES, AND SELENIDES IN THE REDUCTION OF NITROBENZENE AND THE SELECTIVE HYDROGENATION OF A DIOLEFIN INTO AN OLEFIN

A. M. Rubinshtein, A. A. Dulov, S. G. Kulikov*, and N. A. Pribytkova

In the preceding paper [1] we gave the results of an investigation into the action of nickel, chromium, and mixed zinc-nickel oxides, sulfides, and selenides as catalysts for the decomposition of absolute isopropyl alcohol, and we described the preparation of these catalysts, their physical properties, and their phase compositions. Our study of the activities of these catalysts has been extended also to the selective hydrogenation of one double bond of a diolefin ($C_4H_6 + H_2 \longrightarrow C_4H_8$) and to the vapor-phase reduction of nitrobenzene to aniline ($C_6H_5NO_2 + 3H_2 \longrightarrow C_6H_5NH_2 + 2H_2O$). The present paper is devoted to a description of this investigation and a discussion of the results together with data obtained on the decomposition of isopropyl alcohol.

EXPERIMENTAL

From reported data on nickel sulfide catalysts [2] it is known that the hydrogenation and reduction reactions that we have selected proceed readily under high pressures and can be brought about also at ordinary pressure. Hence, in carrying out the experiments at ordinary pressure, we employed low space velocities of reactants over the catalyst so as to ensure an adequate degree of conversion. The experiments were carried out over separate, fresh portions of the catalysts described and characterized in the previous paper [1]. Determinations of the phase compositions of the catalysts by the X-ray structure method both after the hydrogenation and after the reduction reactions gave the same results for all the catalysts, except NiO and chromium selenide, as those obtained after the decomposition of isopropyl alcohol over these catalysts. The phase compositions of NiO catalysts after hydrogenation or reduction reactions in the present investigation differed from before in that no $Ni(OH)_2$ and metallic nickel crystalline phases were detected. After the experiments on the hydrogenation of butadiene, the crystalline phases Cr_2O_3 and CrSe were detected, although the original catalyst and catalysts used in the decomposition of the alcohol and in the reduction of nitrobenzene were amorphous to X-rays.

Catalytic Reduction of Nitrobenzene

All the catalysts were subjected to identical conditions. The catalyst (5 ml) was placed in a V-shaped quartz reactor [3]. This was heated in a vertical block electric furnace, the temperature of which was controlled with an electronic regulator. Nitrobenzene was passed through at a uniform rate of 0.04 liter per minute (space velocity 0.24 $hour^{-1}$; it was supplied through a calibrated automatic dosimeter), and hydrogen, purified from traces of moisture and oxygen, was passed in at the rate of 15 ml (STP) per minute, i.e. 11-12 mole-% excess. Each catalyst was investigated at three temperatures— 220°, 260°, and 300°—after which a control experiment was carried out at 260°. In some cases supplementary experiments were carried out in intermediate regions, and even (in the case of ZnO) at higher temperatures. The temperature in the center of the layer of catalyst was measured by means of a thermocouple.

*Deceased.

TABLE 1

Degree of Conversion of Nitrobenzene into Aniline*

Temperature (°C)	Degree of conversion (%)								
	NiO	NiS	NiSe	NiO — ZnO	NiS — ZnS	NiSe — ZnSe	Cr_2O_3	CrS	CrSe
220	1.5	13.6	2.4	0	0	0	1.1	2.2	5.1
240	3.7	25.4	—	—	—	—	—	—	—
260	7.3	27.1	12.6	0	3.8	0	2.3	2.2	7.0
280	24.2	—	—	—	—	—	—	—	—
300	47.5	20.3	7.7	2.0	5.6	4.4	4.6	3.5	14.0
240(repeat)	6.6	10.1	—	—	—	—	—	—	—
260 "	—	—	2.3	0	2.4	3.2	2.2	2.2	6.3

* Zinc compounds are not included in the table because they were found to be quite inactive at 220-300°, with the exception of ZnSe, which gave 1.9% conversion at 300°. At 350° ZnO gave only 1.2% conversion.

TABLE 2

Specific Activities of Catalysts for the Reduction of Nitrobenzene*

Temperature (°C)	Specific activity								
	NiO	NiS	NiSe	NiO — ZnO	NiS — ZnS	NiSe — ZnSe	Cr_2O_3	CrS	CrSe
220	0.40	3.02	0.23	0	0	0	0.27	0.63	0.93
240	0.99	5.65	—	—	—	—	—	—	—
260	1.95	6.10	1.23	0	3.45	0	0.57	0.63	1.27
280	6.45	—	—	—	—	—	—	—	—
300	12.85	4.50	0.75	2.0	5.10	2.51	1.15	1.0	2.67
240(repeat)	1.76	2.25	—	—	—	—	—	—	—
260 "	—	—	0.22	0	2.18	1.77	0.55	0.63	1.14

* See note to Table 1 regarding zinc compounds.

The aniline content of the reaction product was determined by titrating the acidified catalyzate with sodium nitrite solution [4]. The activities of the catalysts were estimated from the extent of the conversion of nitrobenzene into aniline (Table 1), and were expressed also in the form of specific activity [degree of conversion (%) per gram of catalyst, Table 2]. The specific activity per unit volume can be found from the data in Table 1 by division by 5 (volume of catalyst in milliliters).

In an examination of Tables 1 and 2 the good reproducibility of the results on chromium catalysts should be noted. The repeat experiment at 260° was carried out after the 300° experiment. Satisfactory reproducibility was generally observed for mixed Ni-Zn and NiO catalysts, but it was poor for NiS and NiSe (lower activity in the repeat experiment), probably owing to the change in phase composition in these catalysts [1].

The experimental results show that the metal compounds contained in the catalysts can be placed in the following series of diminishing activity: Ni > Cr > Zn. The variation of specific activity with temperature is represented in Fig. 1 (a, b, and c) for all except the zinc catalysts. In the mixed catalysts, the addition of zinc compounds to nickel compounds results in appreciable diminution in activity, as compared with straight nickel catalysts: under the given conditions zinc compounds act as inert carriers.

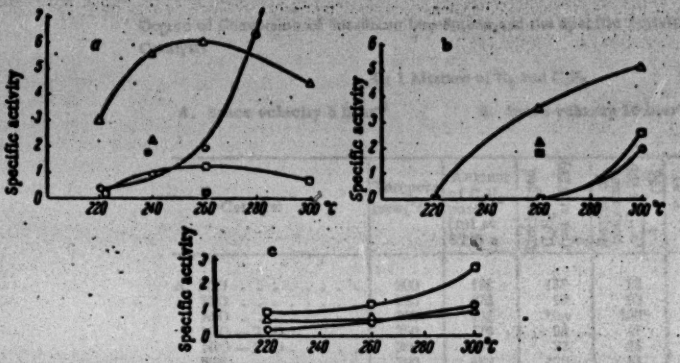

Fig. 1. Dependence of the specific activities of the catalysts on temperature: a) nickel catalysts; b) nickel-zinc catalysts; c) chromium catalysts; □) oxides; △) sulfides; □) selenides; the black points refer to repeat experiments).

The nickel compounds fall in the following series in order of diminishing activity: S > Se > O. It is here important to note that the specific surface of NiS (6.4 sq.m/g) was considerably less than those of NiO (24 sq.m/g). and NiSe (27 sq.m/g). The curves for the change of activity with temperature show that nickel selenide and sulfide become less active with rise in temperature, whereas NiO becomes much more active (probably owing to partial reduction to metallic nickel on the surface, though this could not be observed as a crystalline phase). The reduction in the activities of sulfide and selenide may be due to two causes: 1) their partial oxidation by nitrobenzene—which the comparatively low excess of hydrogen in the system may not be able to prevent—with formation of oxide or sulfide; 2) transformation of NiS and NiSe into Ni_3S_2 and Ni_3Se_2.

Mixed Ni-Zn catalysts form the same activity series as the straight nickel catalysts. Chromium catalysts form the activity series Se > S ≈ O, and their specific surfaces were 38, 190, and 25 sq.m/g respectively. Nevertheless, the sulfide and oxide were approximately equally active, and less active than the selenide.

Selective Hydrogenation of Butadiene to Butene

A gas mixture consisting of 75% of electrolytic hydrogen and 25% of butadiene was passed from a gas meter to a drying column filled with solid caustic soda, and then to a reactor containing 5 ml of catalyst, which was placed in a vertical block electric furnace, the temperature of which was controlled by means of a contact galvanometer. The experiments were carried out in the temperature range 200-300° for 1-2 hours at space velocities of 5 and 10 hour^{-1}. The gaseous reaction products were collected in a calibrated gas holder over saturated brine. Gas volumes were reduced to STP. The amounts of butadiene in the original mixture and in the gaseous products was determined, accurate within 0.5%, in a Bushmarin apparatus (absorption with maleic anhydride). The amounts of diolefins and olefins in the gaseous products were determined also by absorption with mercuric sulfate solution. Butane was determined by combustion over copper oxide in a GIAP (State Institute of the Nitrogen Industry) apparatus. The degree of conversion of the butadiene was calculated from the difference between the amount of butadiene passed in and the amount that remained unchanged. The experimental results are given in Table 3.

It must be pointed out that at 250° NiO gave appreciable conversion of butadiene into butane, whereas at 225° butane was not formed in appreciable amounts and hydrogenation proceeded selectively with formation of butene. Three successive experiments with one sample of NiS at 250° showed that the activity of the catalyst changed considerably with time: the degree of conversion diminished from 88% in the first experiment to 57% in the third. Comparison of this result with the change in phase composition of the catalyst enables us to infer that the reduction in activity is associated with the accumulation of Ni_3S_2 in the catalyst.

TABLE 3

Degree of Conversion of Butadiene into Butene and the Specific Activities of the Catalysts

4 : 1 Mixture of H_2 and C_4H_6

A. Space velocity 5 hour^{-1} B. Space velocity 10 hour^{-1}

	Catalyst	Temperature (°C)	Amount of C_4H_6 passed (ml at STP) a	Unchanged C_4H_6 (ml at STP) b	Degree of conversion $\frac{a-b}{a} \times 100$ (%)	Specific activity
A.	NiO	200	178	138	22	5.7
	NiO	225	178	19	90	23
	NiO	250	232	Hor	100*	25.8*
	NiO — ZnO	250	176	94	47	47
	NiO — ZnO	300	194	32	84	84
	NiS	200	482	229	53	11.8
	NiS	225	441	38	91	20
	NiS	250	492	59	88	19.6
	NiS	250	406	118	71	15.8
	NiS	250	421	180	57	12.6
	ZnS	250	223	182	18	0.7
	ZnS	300	502	473	6	2.2
	NiS — ZnS	250	245	157	36	32.5
	NiS — ZnS	300	334	111	70	64
	CrS	250	259	109	58	16.8
	NiSe	250	221	27	88	8.8
	NiSe	200	241	96	60	6
	NiSe — ZnSe	250	239	115	52	31
	ZnSe	250	217	187	14	3.3
	ZnSe	300	326	269	14	3.3
	CrSe	250	378	14	96	17.3
B.	NiO	200	177	143	20	5.2
	NiO — ZnO	250	177	153	14	14
	NiS	250	173	50	71	15.8
	NiS — ZnS	300	314	149	53	48
	NiSe	250	221	32	85	8.5
	NiSe	300	181	107	41	4.1
	NiSe — ZnSe	250	239	188	22	12.2
	CrS	250	239	144	40	11.4
	CrSe	250	398	44	90	16.4

* The reaction product contained 60 ml of butane, which corresponds to 25% of the original butadiene.

As in the reduction of nitrobenzene, in the hydrogenation of the double bond zinc catalysts were of very low activity. Chromium catalysts were highly active. Comparison of results obtained at space velocities of 5 and 10 hour^{-1} shows that this increase in space velocity has little effect on the degree of conversion for CrSe (250°), NiO (200°), NiS (250°), and NiSe (250°). With respect to specific activity in the hydrogenation of butadiene to butene, the metal oxides, sulfides, and selenides fall in the series Ni > Cr > Zn, i.e. their behavior is similar to that found in the reduction of nitrobenzene and in the decomposition of isopropyl alcohol [1]. With respect to specific activity in the hydrogenation of butadiene (Table 3), the nickel compounds fall in the series NiS > NiSe > NiO (with the exception of NiO at one temperature (250°), at which hydrogen was no longer selective and resulted in the formation of much butane).

The mixed Ni-Zn sulfide catalyst was also more active then the selenide: the activities of these catalysts are clearly determined by the nickel compounds. Chromium selenide was more active than the sulfide, which is particularly evident from their specific activities at 250° at a space velocity of 10 hour^{-1}.

Discussion of Results

The activities of the investigated catalysts in the reduction of nitrobenzene and the hydrogenation of a diolefin have been compared above, and for the decomposition of isopropyl alcohol this comparison was done in the preceding paper [1]. It must be emphasized that, as the phase compositions of the catalysts changed in the course of the experiments, we were cautious in our approach to an estimate of comparative activities, basing our views mainly on initial activities, as being more reliable: in the first short experiments phase transformations could not proceed very far and have any considerable effect. It should be noted that in all of our experiments there was a reduction in activity as we passed from compounds of Group VIII metals to those of Group II metals, and the sequence for the oxide, sulfide, and selenide of each metal was the same in the hydrogenation and reduction reactions. Some exceptions found for the decomposition of an alcohol [1] were apparently attributable to the fact that in this case reactions of a different type were occurring, namely, dehydration and dehydrogenation.

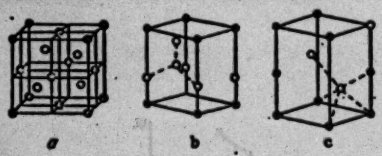

Fig. 2. Elementary cells: a) sphalerite; b) wurtzite; c) nickel arsenide.

For the correlation of activity with catalyst structure it is important to note that the sulfides and selenides that we have investigated have coordinated structures with homeopolar (α- and β-ZnS) or metallic bonds (NiS, NiSe, and others). In crystals of sphalerite (Fig. 2 a) and wurtzite (Fig. 2 b) the coordination of Zn with respect to S and of Se with respect to Zn is quaternary. Nickel and chromium sulfides and selenides belong to the nickel arsenide type (Fig. 2 c) with coordination numbers of the metal atom with respect to S (or Se) and of S (or Se) with respect to the metal atom of 6 [5].

As in each of the series of compounds investigated the metal remains the same, it was natural to compare the activities with the covalent radii of the nonmetals (O–0.66; S–1.04; Se–1.17 A [5]), the covalent radius of the metal being regarded as constant. This has been done in Fig. 3 for the reduction of nitrobenzene over nickel and chromium catalysts. We may point out that, although the extent of conversion is not great, the activity sequence of oxide, sulfide, and selenide cannot be fortuitous, for it is preserved at all temperatures and, moreover, is identical for nickel and mixed Ni-Zn catalysts. In the series of nickel compounds, the sulfide was most active, whereas in the chromium series the selenide was most active—although it might be supposed that the variation in activity should be the same in both series. This contradiction, however, is only apparent: bivalent nickel bound with six electron pairs at the corners of a tetrahedron has a covalent atomic radius of 1.39 A [6], whereas under similar circumstances chromium has a covalent atomic radius of 1.22 A (extrapolation of data from [7] to a coordination number of 6). Hence, in the compounds under consideration the atomic radius of Ni is greater than that of Cr by 0.17 A, which is very little different from the amount by which the covalent radius of Se is greater than that of S.

Thus, the differences between the radii of the metals and the radii of the nonmetals are mutually compensating, and the Ni-S distance in the NiS lattice is equal to the Cr-Se distance in the chromium selenide lattice. Hence, in each of the series of compounds represented in Fig. 3, the highest activity is possessed by a compound having a given M-X interatomic distance, namely 2.40-2.43 A, which gives striking confirmation of the principle of structural correspondence in the multiplet theory of catalysis [8]. The distinctive chemical nature of the chemical compound is manifested not in the relative activity (in the oxide, sulfide, selenide series), but in the magnitude of the activity, i.e. the degree of conversion.

As already stated, the degree of conversion is greater for nickel compounds than for chromium compounds.

The inference that we have just made concerning the part played by the structural factor is confirmed also by results obtained for the hydrogenation of one double bond of butadiene: NiS is more active than NiSe, and CrSe is more active than CrS. This is not surprising, for the difference between the interatomic distances C=C (1.33 A) and N=O (1.21 A) [9] is not great. The structural factor, i.e. the ratio of the interatomic distances in the reacting molecule and in the catalyst surface, must be approximately the same in both reactions. The effect of the structural factor can be judged also from Table 4 showing the results obtained on sulfide catalysts for the three reactions investigated [the figures for isopropyl alcohol—amount of hydrogen and propene (ml) per 1 ml of alcohol and 10 ml of catalyst; for the other two reactions—degree of conversion (%)]:

TABLE 4

	NiS	CrS	ZnS	NiS – ZnS
Decomposition of i-C_3H_7OH at 245°	64.4	22.4	0	3.6
Decomposition of i-C_3H_7OH at 295°	256.9	128.2	122.6	270
Reduction of $C_6H_5NO_2$ at 300°	20.3	3.5	0	5.6
Hydrogenation of C_6H_6 at 250°; space velocity 5 hour^{-1}	87.5	48.4	16.1	39.0
Constants of crystal lattice (A)				
a	3.42	3.44	3.84	—
c	5.30	5.67	6.28	—

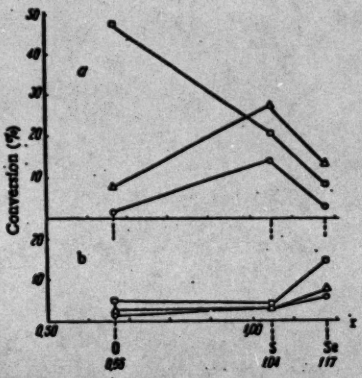

Fig. 3. Dependence of catalyst activity on the covalent radius of the nonmetal: a) nickel catalysts; b) chromium catalysts; o) at 220°; Δ) at 260°; □) at 300°.

In these data we can clearly see the parallelism between activity and lattice characteristics: the most favorable interatomic distance for the accomodation of the reacting molecule on the surface is found in the NiS lattice, and the least favorable in the ZnS lattice. As the parameters of the lattice increase, the activity of the catalysts diminishes. This, of course, can be attributed to the geometry of the surface, which can be regarded as a function of the chemical nature of the catalyst.

In connection with these considerations, it is desirable to examine the effect of the structural factor on selectivity in the decomposition of an alcohol [1]. Since oxygen, sulfur, and selenium belong to the same group of the periodic system and the investigated compounds of these elements are isomorphous with the exception of cubic NiO, the difference between the orientation of the alcohol molecule on the surface by means of the CHOH group for dehydrogenation and by means of the CH_3CHOH group for dehydration must be determined mainly by the interatomic distances on the catalyst surface, for the possibility of one or the other disposition of the reacting molecule must depend on these distances. Energetic differences, on the other hand, must result in different rates of conversion in the given direction. In our case the M-X distance increases from the oxide to the selenide. As shown in the previous paper [1], the selectivity coefficients are Cr_2O_3 0.63, CrS 0.39, and CrSe 0.03, i.e. dehydration becomes more marked with increase in the interatomic distances on the catalyst surface. This occurred both on zinc and on nickel catalysts, though in the last case evolution of hydrogen sulfide and the transformation of NiS into Ni_3S_2 had considerable influence on the process. Our results are in close accord with those obtained previously for MgO [10], TiO_2 [11], Nb_2O_5 and Ta_2O_5 [12] on the effect of interatomic distance on selectivity and with theoretical considerations relating to these results [10, 11].

As the effect of the geometric factor is in evidence in the cases we have investigated, we may conclude that the reactions proceed by a doublet mechanism, not only on oxides, but also on sulfides and selenides. From the fact that activity is directly related to the interatomic distance between metal and nonmetal on the surface, we may conclude that nonmetal atoms form part of the active center and participate in the formation of the multiplet complex.

SUMMARY

1. Data was obtained on the relative activities of oxides, sulfides, and selenides of nickel, zinc, and chromium and of the corresponding mixed Ni-Zn catalysts in the reduction of nitrobenzene to aniline and the selective hydrogenation of one double bond of a diolefin.

2. It was found that in both reactions the activity falls in the sequence Ni > Cr > Zn, i.e. from compounds of the Group VIII metal to compounds of the Group II metal. Zinc catalysts were of low activity under the experimental conditions, nickel catalysts fell into the series NiS > NiSe > NiO with respect to specific activity, and for the chromium catalysts the sulfide was less active than the selenide.

3. The relationship between the activities of the catalysts, on the one hand, and their phase compositions and structures, on the other, was examined, and it was shown that the observed changes in activity and selectivity in the series oxide, sulfide, selenide are satisfactorily explained on the principle of structural correspondence of the multiplet theory of catalysis, which has again been confirmed by the results now obtained.

4. It was suggested that nonmetal atoms take part in the formation of doublets and of the multiplet complex on catalyst surfaces.

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CHEMICAL CHANGES PRODUCED IN THE CELLULOSE MACROMOLECULE BY OXIDIZING AGENTS

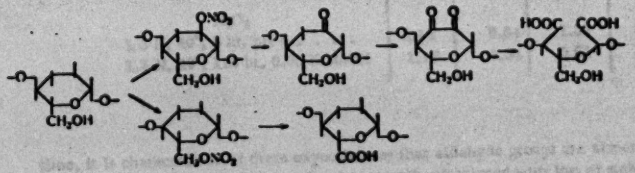
COMMUNICATION 11. CAUSES OF THE CHEMICAL INSTABILITY OF CELLULOSES OXIDIZED WITH NITROGEN DIOXIDE

E. D. Kaverznova and S. A. Kist

It is well known that cellulosic materials, when subjected to the action of moisture, light, and various chemical agencies, undergo oxidative changes that result in a deterioration of mechanical properties and chemical stability. The oxidation of cellulose by nitrogen dioxide is associated with a particularly great change in its properties, and this behavior has not yet found an explanation in the chemical changes brough about by the oxidation. It is characteristic of such oxidized preparations that their mechanical properties deteriorate fairly rapidly with keeping and they break down readily in an aqueous alkaline medium, in spite of their fibrous structure, which cannot be distinguished visibly from that of untreated cellulose. Both these phenomena indicate breakdown of the macromolecular chain under the influence of the new functional groups formed during the oxidation. In the present investigation an attempt was made to relate the instability of these oxycelluloses to peculiarities of their chemical structure.

EXPERIMENTAL

Our previous investigations [1] showed that in the oxidation of cellulose by nitrogen dioxide not only carboxyl groups are formed, but also keto groups. Nitric esters are formed as intermediate compounds, and these then undergo oxidative hydrolysis. Some of the keto groups are oxidized further with rupture of a C—C link in the pyran ring and formation of nonuronic carboxyls. Practically no aldehyde or carbonic ester groupings are formed, and no peroxy compounds could be detected. The reactions occurring can be represented as follows:



The contents of the individual functional groups change very greatly as oxidation proceeds. Table 1 gives analyses of several freshly prepared oxycelluloses differing in degree of oxidation.

A characteristic of oxidation by nitrogen dioxide is the high content of new functional groups in the oxidized cellulose. This result is favored by the fact that reaction occurs in an atmosphere of the gas and hydrolytic processes are absent. In nitrogen dioxide oxidation the yield of oxycellulose is close to theoretical value (105-115%

on the original weight), whereas in oxidations with hypochlorite and other oxidizing agents in an aqueous medium the yield of oxycellulose falls as the duration of the oxidation increases. In Table 2 we make a comparison of the contents of functional groups in oxycelluloses prepared by the action of various oxidizing agents.

TABLE 1

Contents of Functional Groups in Oxycelluloses Prepared by Oxidation with Nitrogen Dioxide

Preparation No.	Content (%) of COOH groups	carbonyl groups	aldehyde groups	keto groups	N
33	7.5	1.02	0.02	1.00	0.37
34	9.9	3.04	0.01	3.03	0.43
Series 1	17.2	3.28	0.04	3.24	0.20
Series 2	16.8	2.62	0.07	2.55	0.18

It follows from Table 2 that, in spite of the powerful oxidation brought about by sodium hypochlorite and hydrogen peroxide, the numbers of carboxy and keto groups in the resulting oxycelluloses are very much less than in nitrogen dioxide oxycelluloses. The ratio of keto groups to carboxyls after the oxidation of cellulose with nitrogen dioxide is not high—even less than in hypochlorite and peroxide oxycelluloses—but the absolute number of keto groups is many times greater than in any other oxycellulose.

Thus, high contents of carboxy and keto groups are characteristic of celluloses oxidized with nitrogen dioxide. At the same

TABLE 2

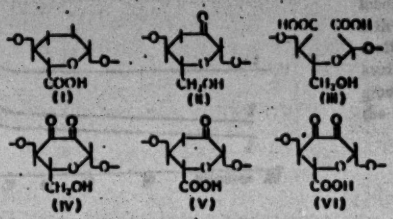
Contents of Functional Groups in Oxycelluloses Prepared by the Action of Various Oxidizing Agents

Oxidizing agent and conditions of oxidation	Amount (equiv. per 100 glucose residues) COOH	keto groups	aldehyde groups	Keto (%) / COOH	Aldo (%) / COOH
NO_2					
5 hr 1 mol NO_2 per glucose residue, 22°	7	0.64	0.23	9	3
96 hr, 4 mol NO_2, 22°	44	15.5	0.23	35.2	0.55
120 hr, 6 mol NO_2, 20°	66	19.9	0.24	30.2	0.4
NaClO					
0.23 N, 25°, 24 hr, pH 3.1	1.66	0.5	1.68	30	101
0.04 N, 20°, 20 days, pH 11.	1.47	1.0	0.17	70	11.6
H_2O_2					
1.5 N, 40°, 5 hr, pH 4	1.15	0.64	1.39	56	121
1.5 N, 40°, 110 hr, 0.05 N NaOH	1.12	0.34	0.61	30	54

time, it is characteristic of these oxycelluloses that aldehyde groups are almost completely absent, whereas it is the presence of aldehyde groups that is generally associated with loss of stability of the cellulose macromolecule [2]. There is therefore no foundation for the view of Nabar and Padmanbhan [3], according to which NO_2-oxidized cellulose readily undergoes breakdown owing to the supposed presence of dialdehyde groupings. It was natural to turn our attention on the high content of keto groups and to elucidate their effect on the chemical properties of the oxycelluloses obtained by nitrogen dioxide oxidation.

We were interested in the effect of keto groups on the hydrolytic splitting of oxycelluloses in alkaline and acid media and on the breakdown that occurs when oxycelluloses are kept. In the oxycelluloses studied the

following functional groups are present, and they might be found in the glucose residues in the combinations indicated in the schemes:



In 1942 Kenyon suggested that the instability of oxycelluloses prepared by oxidation with nitrogen dioxide in an alkaline medium is the result of a great accumulation of electronegative COOH groups in them [4]. This point of view was supported by Rogovin, Kondrashuk, and Malakhov [5]. However, recent observations by Vollmert [6] on free pectic acids containing COOH groups in each galactose residue showed that these acids are quite stable to the action of 1% caustic soda at room temperature. The same conclusion was reached for alginic acid by Nevell [7]. There are no grounds, therefore, for the view that the presence of carboxy groups in the 6-positions of the glucose residues is in itself of significance in determining instability to alkali.

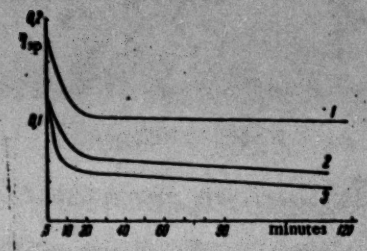
Moreover, the effect of COOH groups at C-2 and C-3 (Form III) on alkaline breakdown cannot be great, for it is known from investigations of Reeves and others [8] and of Yashunskaya, Shorygina, and Rogovin [9], that by the oxidation of the aldehyde groups of "dialdehydocellulose", its stability toward alkalis increases. In the hydrolysis of "dicarboxycelluloses" (0.3-0.6% COOH) in 0.1 N NaOH (24 hours at 90°), the COOH content falls by only 8-9%, whereas in water it falls by 41-64%, i.e. breakdown is only slight in an alkaline medium. Consequently, COOH groups in the 6-, 2-, and 3-positions have no appreciable effect on the stability of the glucoside linkage in an alkaline medium.

Since NO_2-oxidized oxycelluloses contain no aldehyde groups, but many keto groups, they may be considered to be model substances for the elucidation of the effect of keto groups on the properties of cellulose. The rapid breakdown of these oxycelluloses in an alkaline medium is well known. In illustration we show the curves for the fall in viscosity (see Figure) of alkaline solutions of oxycelluloses having the following contents of functional groups:

	COOH (%)	Keto groups (%)	N (%)
Preparation No. 2	12.9	2.32	2.82
Preparation No. 6	12.1	2.94	0.24

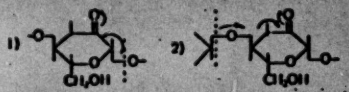
During the first ten minutes there is a sharp fall in viscosity, and after several hours it is no longer possible to precipitate any macromolecular material from the solution. There is every reason to ascribe such a low stability toward an alkaline medium to the keto groups present in the oxycellulose.

The effect of these groups on the stability of the acetal linkage in an alkaline medium has been studied for many compounds of low molecular weight and, in particular, for glucosides [10]. It has been shown that when there is a double bond in conjugation with the keto group [11] or the keto group is in the α- or β-position with respect to the acetal link [12] the stability of this link toward alkali is greatly reduced. The same behavior must be preserved in macromolecular compounds, and an oxycellulose containing a keto group in the α- or β-position to the glucosidic link should have enhanced sensitivity to alkalis.



Fall in viscosity for solutions of celluloses oxidized with nitrogen dioxide (solvent 0.2 %NaOH; temperature 20°; the first point represents a measurement made 4-5 minutes after the start of dissolution):
1) Preparation No. 6 at a concentration of 0.5%;
2) Preparation No. 6 at 0.4%; Preparation No. 2 at 0.4%.

Several mechanisms have been proposed for the activation of the glucosidic link by the keto group. The electronic interpretation of this phenomenon amounts to the assumption of the formation of a cationoid center on the carbonyl oxygen. The induced shift of a free electron pair from the glucosidic oxygen facilitates the approach of the OH-ion. Hibbert [13] attributes the effect to the acidity of the carbonyl group, it being well known that the higher the acidity, the lower the stability of the glucosidic link.



For oxycelluloses Schemes 1 and 2 are equally probable, since the keto group is simultaneously in an α- and a β-position to a glucosidic link.

It is quite probable that the simultaneous presence of a keto and a carboxyl group in one monomer unit will still further reduce the stability of the glucosidic link. The probability of this simultaneous presence is fairly high, even if we assume uniform oxidation along the whole chain, which is known to be untrue since oxidation by oxides of nitrogen proceeds in a nonuniform fashion. For example, for preparations oxidized to a medium extent and containing 60 carboxy and 18 keto groups per 100 glucose residues, the probability of the simultaneous presence of these groups in one unit is 0.6 x 0.18 = 0.108, i.e. 10 glucose residues out of 100 may contain COOH and CO groups simultaneously.

The direct effect of nitric ester groupings on alkaline breakdown need not be considered here, since the number of these groupings is small in normally oxidized preparations, being 1-4 per 100 glucose residues (0.1-0.3% N). When these groups are hydrolyzed in an alkaline medium, some keto groups should be formed in addition to those already present, but they will not produce substantial changes in the properties of the preparation.

Hence, from an examination of the effect of functional groups on the stability of the glucosidic link in an alkaline medium we may infer that the most notable effect is to be attributed to keto groups and may possibly be reinforced by carboxyls present. Whereas we have a well grounded explanation of the alkaline instability of oxycelluloses prepared by the action of nitrogen dioxide based on the effects of numerous keto groups, the reduction in the stability of these oxycelluloses in an acid medium is much less readily understood. Let us consider the facts. Our experiments on the hydrolysis of oxycelluloses in an aqueous medium (pH 3-4) and in presence of sulfuric acid (3.7 N) have shown that the rate at which these preparations undergo hydrolytic breakdown varies with the extent of oxidation. Slightly oxidized preparations pass into solution just as slowly as unoxidized cotton; with increase in degree of oxidation, dissolution and hydrolysis rates increase in proportion to the extent of oxidation and are several times as high as the rate of dissolution of unoxidized cellulose, as can be seen from Tables 3 and 4.

In the hydrolysis, the highly oxidized part of the chain passes preferentially into solution, so that the remaining, undissolved part of the oxycellulose is less oxidized than the original. In th solution these products of low molecular weight undergo further hydrolysis to monomers. In acid hydrolysis there is also a lowering of nitrogen content owing to hydrolysis of nitric ester groups. It should be noted that the losses in COOH groups and nitrogen were approximately equivalent for the two preparations studied, irrespective of the different original contents of nitrogen in the preparations. All the analyses for funtional groups were carried out by the method described previously [1].

TABLE 3

Hydrolysis of Oxycelluloses in Water and Acids

Preparation No.	Conditions of hydrolysis of oxycellulose	Amount of substance passing into solution	COOH content (%) of original preparation	COOH content (%) of residue	COOH content (%) of solution	Aldehyde content of substance in solution (%)
27	Water, 1 hr, 100°	1	2.53	2.32	17.6	–
20	Water, 1 hr, 100°	17	8.92	6.70	14.7	5.9
20	Water, 3 hours 100°	26	–	–	–	7.7
20	3.7 N H_2SO_4, 1 hr, 100°	32	–	–	–	15.25
Unoxidized cotton	2.5 N HCl, 1 hr, 105°	12	–	–	–	–

The lower the extent of oxidation of the preparation, the more selective is the elimination of oxidized glucose residues from it. For example, in Preparation No. 27 (2.53% COOH) the water-soluble fraction contained 17.6% COOH, and in Preparation No. 20 the fraction passing into solution contained 14.7% of carboxyls, i.e. it contained more unoxidized glucose residues.

All this indicates that the hydrolytic breakdown of oxycelluloses proceeds primarily at the oxidized units of the cellulose chain and that the rate of breakdown is greater for oxycelluloses than for the unoxidized cellulose.

TABLE 4

Passage of Nitrogen and Carboxy Groups into Solution in the Acid Hydrolysis of Oxycelluloses •

(5 g of oxycelluloses was heated in water for 1 hour at 100°)

Preparation No.	Content (equiv. per 100 glucose residues) of		Amount of substance passing into solution (%)	COOH content (mmoles)					Nitrogen content (mmoles)			
	COOH groups	N atoms		in original a	in residue b	in solution a−b	by direct titration	COOH passing into solution (% on original)	in original	in residue	in solution	Nitrogen passing into solution (% on original)
27	91	14.5	1	2.81	2.62	0.19	0.195	6.9	4.27	3.57	0.26	6.1
20	33	5.	17	9.91	6.18	2.73	2.78	28.0	1.57	0.65	0.50	31.7

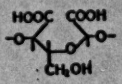
• In the hydrolysis carboxylic acids and HNO_3 or HNO_2 pass into solution. It is therefore not altogether clear why the results of direct titration of acidity after hydrolysis (i.e. COOH + NO_3^-) should coincide with the amount of COOH in solution as determined from the difference in the COOH contents of the original preparation and the residue after hydrolysis. It is possible that decarboxylation occurs, and this compensates for the rise in acidity due to nitrous acid.

What chemical changes occurring during oxidation and what functional groups are responsible for the reduced stability of oxycelluloses in an acid medium? There are few data in the literature on this matter. For pectic and alginic acids in an acid medium (20% HCl at 60°) the hydrolysis rate constants have been found to have the same order of magnitude as the constant for cellulose [14].

	$K \cdot 10^3$ (hour^{-1})
Pectic acid, pH 0.3, 70°	13.1 [15]
Pectic acid, 20% HCl, 60°	14.0 [16]
Cellulose, 20% HCl, 60°	12.0 [16]

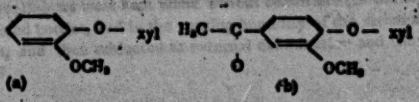
It appears that a COOH group in the 6-position does not affect the properties of the glucosidic link in an acid medium. For "noncarboxycelluloses" oxidized to the extent of 20% COOH, Konkin, Smirnova, and Rogovin [16] also did not find any increase in the hydrolysis rate constant. However, these experiments are not altogether convincing owing to possible errors of method. In these experiments the rate of hydrolysis was followed by determining the increase in the number of aldehyde groups in solution by the iodometric method. In this case the number of aldehyde groups found might not correspond to the course of the breakdown of the oxycellulose macromolecule for the following reasons: 1) breakdown might occur without formation of aldehyde groups, for it might occur at oxygen bridges in opened pyran rings; 2) the hydroxy and keto aldehydes formed in the hydrolysis of strongly oxidized preparations rapidly undergo further reactions with loss of aldehyde groups when heated in an acid medium. Hence, the hydrolysis rate constant based on aldehyde contents does not characterize the actual processes occurring.

We must consider separately the possibility of breakdown in an acid medium at the opened pyran rings referred to above:



Jackson and Hudson [17] examined the behavior of diglycolic acid, obtained by the oxidation of cellulose with hypobromite, and they demonstrated the low stability of the oxygen bridge in this compound: it was broken down by boiling for two hours with water (which would form a slightly acid medium). Hence, when such oxygen bridges occur in oxycelluloses, breakdown of the macromolecular chain may occur as a result of the hydrolytic rupture of these bridges. The experiments of Rogovin, Kondrashuk, and Malakhov [5] offer some possibility of estimating the extent of this breakdown. They compared the stabilities to hot water, i.e. an acid medium, of two samples of oxycelluloses in which COOH groups were present in equal amount (2.8%) but in different positions: in the 6-positions of the glucose residues of cellulose oxidized with nitrogen dioxide, and in the 2- and 3-positions in a preparation obtained by successive oxidation with sodium periodate and with chlorine dioxide. Heating with water at 100° for three hours had almost no effect on the strength and extensibility of the second preparation, but broke down the NO_2-oxidized preparation to a powder. Hence, if oxygen bridges in opened glucose residues cause chain breakdown, then in oxycelluloses prepared by oxidation with nitrogen dioxide there are some other, very much more potent factors contributing to breakdown. The authors consider this factor to be the presence of the carboxyl in the 6-position, a view that is in conflict with the results of Konkin and others.

The oxycellulose preparations studied by Rogovin and coworkers [18] differed not only in the positions of the carboxyl groups in the glucose residues, which, as we have seen, are not of determining significance for the rate of hydrolysis; they differed also with respect to the presence of keto groups, which are present in NO_2-oxidized cellulose, but absent in "dicarboxycellulose" [1]. It is therefore necessary to examine how this group can affect the stability of the glucosidic link in an acid medium. The work of Fisher, Hawkins, and Hibbert [13] may be cited here: this showed that a carbonyl group in the para position to a phenolic hydroxyl in the aglycon has little effect on the hydrolysis of the glycosidic link.



(a) (b)

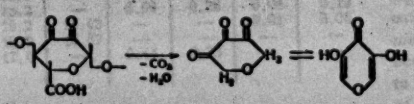
In 0.1% sulfuric acid at 100°, the half-life of (a) is 15 minutes and that of (b) is 20 minutes. The hydrolysis rate constant of turanose (3-α-glucosylfructose) in an acid medium is of the same order as the constant for maltose (4-α-glucosylglucose) $K_{aH} \cdot 10^5$ (sec^{-1}) is 11.9 for turanose and 16.8 for maltose [19].

Hence, no direct effects of carboxyl and keto groups on the stability of oxycelluloses in an acid medium have been established. The question of their effect when present simultaneously in a single glucose residue of the macromolecule remains open.

Nevertheless, it remains a fact that breakdown during heating with water is much more intense for preparations that have been particularly severely oxidized. It is most probable that the cause of the comparatively ready passage into solution of oxycelluloses obtained by the action of nitrogen dioxide, when these are heated in an acid medium, is not isolated activation of glucosidic links in the presence of some particular functional group, but the simultaneous operation of several factors.

It is now almost universally considered that the main cause of the difficulty with which cellulose is hydrolyzed lies in its physical state — the packing of the macromolecular chains, these being bound together by a large number of hydrogen bonds, which hinder hydrolysis. In the course of oxidation, particularly the severe oxidation produced by nitrogen dioxide, hydrogen bonds must be broken and rearranged, and the uniformity of packing must be disturbed. As a result, weak places must appear in the macromolecule. This will facilitate the swelling of the oxycelluloses in water and hydrolytic breakdown in the places modified by oxidation. The extent to which the disturbances in the structure may proceed can be judged from the fact that, when the oxidized preparation contains 17% COOH, of the 300 OH groups present in 100 glucose residues, about 80 have been transformed into other functional groups.

The greater the extent of the oxidation, the greater will be the disturbance in the packing of the macromolecules and the more numerous will be the monomer units that contain both COOH and CO groups, i.e. chemically weakened places. The existence in our oxycelluloses of severely oxidized units containing both carboxy and keto groups appears still more likely in the light of recent work by Battenberg and Berg [20], who hydrolyzed NO_2-oxidized cellulose (13% COOH) with water in a CO_2 atmosphere under pressure and obtained a 3% yield of 3,5-dihydroxy-4H-pyran-4-one. This compound could be formed from a severly oxidized glucose residue of the oxycellulose in the following way:



Hence, in order to explain the breakdown of oxycelluloses in an acid medium it is necessary to take at least three factors into account: the disturbance of the order in the supermolecular structure of the macromolecules in the cellulose fiber arising from its oxidation; the chemical effect of COOH and CO groups in one monomer unit on the glucosidic link; and the formation of unstable units made up of opened rings.

Our efforts to find the causes of the breakdown of oxycelluloses during storage led to more definite results. The results of some experiments that we have carried out can be regarded as a proof of the effect of keto

groups on the chemical stability of oxycelluloses during storage. These experiments were briefly as follows: samples of oxycelluloses were kept under various conditions (in the dry state over calcium chloride, in the air-dry state in closed bottles, and in the varying humidity of the atmosphere) for periods of from 6 months to 2 years 6 months, and then subjected to external examination and chemical analysis. The results are given in Tables 5 and 6.

TABLE 5

Outward Changes in Oxycelluloses during Storage

Preparation No.	Chemical composition	Duration of storage (years)	Conditions of Storage		
			in a desiccator	in the air-dry state	in the atmosphere
1	8.2% COOH 4% N	2.5	White, fibrous, does not rub into a powder	Brown, fibrous, rubs into a powder	Brown, partially falls to a powder
7	12.5% COOH	2.5	Cream, fibrous, not readily pulverized	Yellow, fibrous, readily pulverized	Reddish, very friable, partially falls to a powder
14	16.2% COOH 0.1% N	1.5	White; fibers strong		Reddish, fiber falls to a powder

TABLE 6

Chemical Changes in Oxycelluloses during Storage in the Air-dry State

Preparation No.	Time of keeping (months)	Content, before and after storage					
		COOH groups (%)		N (%)		aldehyde groups (%)	
		before	after	before	after	before	after
18	6	13.50	14.6	0.13	0.16	—	1.05
15	6	13.55	—	—	—	0.02	0.21
32	6	17.2	—	0.2	—	0.04	0.57
1	12	8.2	—	4	0.78	—	1.25*
7	15	12.5	12.75	—	—	—	—
9	14	15.2	—	0.66	0.26	0.06	0.19
14	14	16.2	16.43	—	—	0.01	0.04
14	14	16.2	16.67	—	—	—	—
4	15	17.4	—	0.44	0.33	—	—

* Kept for 34 months.

Two main conclusions follow from Table 6: 1) in presence of moisture, breakdown of oxycellulose macromolecules occurs, this being manifested in change of color and mechanical strength and the appearance of new aldehyde and carboxyl groups; the nitrogen content falls to 0.1÷0.2%; 2) in absence of moisture the breakdown of oxycelluloses is almost completely prevented.

In the storage of oxycelluloses it is possible that hydrolytic breakdown can occur under the influence of the acidity created by the COOH groups themselves. This possibility is discussed in a paper by Davidson and Standing [21], who found that, after celluloses oxidized with hypobromite in an alkaline medium and containing 0.4-1.5% COOH had been kept for 12 months, divergencies began to appear in the results of the determination of carboxy groups by the calcium acetate method and the methylene blue method. The authors considered that autohydrolysis occurred and some of the carboxy groups present in the breakdown products of low molecular weight went into solution during the methylene blue determination and could therefore not be determined. It is true that the amount was very small (0.009-0.09% COOH). Our qualitative observations show that the breakdown of NO_2-oxidized celluloses is determined by other causes, for partially neutralized preparations of lower acidity were less stable to storage than preparations containing free carboxy groups. Observations on pectic substances and other polyuronic acids, which are stable to keeping, also did not confirm the suggestion that there is an

appreciable effect attributable to autohydrolysis of oxycelluloses due to their own acidity. We were unable to establish any relationship between the contents of nitric ester groupings in oxycelluloses and the rates of breakdown during keeping.

In order to determine the effect of keto groups on breakdown during keeping, the following experiment was carried out. The oxycellulose was treated with hydroxylamine in a weakly acid medium in order to block carbonyl groups, washed until reaction for hydroxylamine in the washings was negative, dried, and allowed to lie in the air-dry state. The experimental results (Table 7) show that, in spite of the presence of moisture, oxycellulose with blocked carbonyl groups preserves its color and mechanical properties for 2 years 6 months. The main chemical index of breakdown the content of aldehyde groups— changed insignificantly as compared with its increase in the preparation kept in the untreated condition. This experiment shows that carbonyl groups —in our case keto groups—form the main factor determining breakdown in the air in a weakly acid medium. Blocking of the carbonyl groups makes preparations stable to keeping irrespective of the presence of moisture.

TABLE 7

Comparison of Changes during Storage in Oxycelluloses having Free and Blocked Keto Groups

Preparation No.	Original analysis	Duration of Storage	Condition after storage in air-dry state	
			with free keto groups	after conversion into oxime
2	12.9% COOH 2.82% N, 0.5% aldehyde groups	2.5 years	Brown, rubs into a powder; 1.4% aldehyde groups	Cream, fibrous, fiber has some strength; 0.18% aldehyde groups
1	2.5% COOH	5.5 years	Brown, friable	Cream, fibrous; 0.43% aldehyde groups

No neutralization of carboxy broups occurred in the treatment with hydroxylamine, since the reaction was carried out in an acid medium. The carboxy groups in the hydroxylamine-treated preparations remained free, but the oxycelluloses were not degraded. It follows that autohydrolysis of the oxycelluloses as a result of their own acidity is only of secondary importance. Breakdown occurs as a result of change in the chemical stability of the glucosidic link brought about by the presence of a keto group. Whether this breakdown is hydrolytic or is associated with oxidative processes involving atmospheric oxygen has not yet been studied. It is most probable that oxidative-hydrolytic breakdown occurs, since the number of carboxyl groups, and apparently also keto groups, increases during keeping.

Hence, it follows from an examination of the changes undergone by NO_2-oxidized cellulose in an alkaline medium, during acid hydrolysis, and during keeping in presence of atmospheric moisture that its chemical stability is very much less than that of unoxidized cellulose. The main cause of this instability to alkali and to keeping in the air is the high content of keto groups in the oxidized preparations. The high tendency for these oxycelluloses to undergo hydrolysis in an acid medium makes its appearance only when oxidation has proceeded to an appreciable extent (at above 2-3% COOH), and it probably depends on the simultaneous effects of several factors, among which the most important may be: the destruction of molecular interaction, the appearance of weak links in the chain owing to the formation of opened pyran rings, and the change in the stability of a glucosidic link between glucose residues that may contain several new functional groups simultaneously.

SUMMARY

1. Oxycelluloses prepared by nitrogen dioxide oxidation are highly unstable in an alkaline medium and readily break down when kept in presence of moisture and air. The higher the degree of oxidation of these oxycelluloses, the more readily do they undergo acid hydrolysis.

2. In absence of moisture, breakdown during storage is greatly retarded.

3. When the keto groups of the oxycelluloses are blocked, degradation during storage stops almost completely whether moisture is present or not.

4. The main cause of the degradation in an alkaline medium is the large number of keto groups present in the oxycelluloses – there may be as many as 15-18 per hundred glucose residues. It is probable that the simultaneous presence of keto and carboxy groups in one monomer unit results in still higher instability in such glucose residues.

5. The main cause of breakdown during storage in the atmosphere in presence of moisture lies in the influence of keto groups, as is shown by the effect of blocking these groups.

6. The hydrolytic breakdown of the oxycelluloses studied under the action of an acid medium is not appreciably accelerated by the presence of only carboxy, or of only keto groups. It is probable that breakdown in an acid medium depends on the simultaneous effects of several factors, which come into being as a result of the oxidation. The most important of these factors may be: destruction of the ordered system of molecular interactions owing to the effect of new functional groups, and, to a less extent, changes, resulting from the presence of these groups, in the chemical stability of the macromolecular chain; some importance must be attached also to modified monomer units consisting of opened pyran rings and severely oxidized glucose residues in which both COOH and CO groups are present simultaneously.

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APPLICATION OF THE IODOFORM REACTION TO THE ANALYSIS OF SOME VINYL COMPOUNDS

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It is well known that compounds containing the group CH_3CO- or CH_3CHOH- readily form iodoform when treated with alkali and iodine [1]. Esafov and Stafeeva [2] showed that α,β-unsaturated ketones also give the iodoform reaction, although neither of these groups is present. Such groups, however, are formed by the hydrolytic splitting of the α,β-unsaturated ketones in presence of alkali:

$$RCH{=}CHCOC_2H_5 + H_2O \rightarrow \underset{\underset{OH}{|}}{RCH}{-}CH_2COC_2H_5 \rightarrow R\overset{\overset{O}{\|}}{C}H + CH_3COC_2H_5 \qquad (1)$$

The hydrolysis products indicated in the equation react with alkali and iodine with formation of iodoform [2].

In the present investigation it was found that the iodoform reaction can be extended to not only unsaturated ketones, but also such substances as vinyl ethers (I) and N-vinyl lactams (II):

$$CH_2{=}CHOR \quad (I), \qquad CH_2{=}CH{-}N\overset{(CH_2)_n}{\diagdown\!\!\diagup}CO \quad (II)$$

in which n = 3, 4, 5.

In this case the formation of iodoform is not associated with the hydrolysis of an unsaturated compound (which could yield acetaldehyde). It is well known, for example, that vinyl ethers are not hydrolyzed in alkaline solutions [3]. As regards vinyl lactams, a special investigation showed the absence of hydrolytic breakdown during treatment with alkali under the conditions of the iodoform reaction (i.e. at room temperature); even when the treatment was for nine hours at 60°, no hydrolysis products could be isolated (Table 2).

We consider that the formation of iodoform from vinyl ethers and N-vinyl lactams (and also, possibly from α,β-unsaturated ketones) is due to direct reaction of the double bond with iodine and alkali. This view is in full accord with the established view on the mechanism of the iodoform reactions of acetone and acetaldehyde. It is considered that in these reactions acetone and acetaldehyde react not in the keto, but in the enol form, the double bond of which combines either with two atoms of iodine formed by the decomposition of hypoiodite, or with hypoiodite itself (compare the addition of hypochlorite to ethylene). A series of successive transformations (through mono-, di-, and tri-iodoacetaldehyde) results in the formation of iodoform. It was proved that substances that are incapable of reaction in the enol form, i.e. do not contain reactive double bonds (e.g. paraldehyde), do not give the iodoform reaction [4].

It is evident that in the case also of vinyl ethers (and N-vinyl lactams), in the reaction with alkali and iodine the primary act is the addition of two atoms of iodine with subsequent breakdown of the α,β-diiodo derivatives (Equation 2), or of KOI with further reaction according to Equation 3:

$$CH_2{=}CHX + I_2 \rightarrow CH_2I{-}CHIX \xrightarrow{H_2O} CH_2ICHO + XH + HI. \qquad (2)$$

TABLE 1

Behavior of some Vinyl Compounds in the Iodoform Reaction

No.	Class of compounds	Formulas of compounds	Positive or negative reaction
1	Alkyl vinyl ethers	$CH_2=CHOR$ (R = $-CH_3$, $-C_2H_5$, $-C_3H_7$-i, $-C_4H_9$, $-C_5H_{11}$-i, $-C(CH_3)_3$, $-C_5H_{11}$-i $-CH(CH_3)CH_2CH_2CH_3$, $-C(CH_3)_2CH_2CH_3$ $-C_6H_{11}$-cyclo	Positive
2	Aryl vinyl ethers	$CH_2=CHOAr$ (Ar = $-C_6H_5$, $-C_6H_4OCH_3$)	Negative
3	Vinyl ethers of glycerol, glycols, and their derivatives	$CH_2=CHO(CH_2)_2OR$ (R = $-CH_3$, $-C_2H_5$, $-CH_2CH_2OH$), $O[(CH_2)_2OCH=CH_2]_2$; $CH_2=CHOCH(CH_2OCH=CH_2)_2$	Positive
4	Vinyl ethers of ethanolamines	$NH_2(CH_2)_2OCH=CH_2$, $N(CH_2)_2OCH=CH_2)_3$, $N(CH_2CH_2OH)_3$, $N(CH_2CH_2OCH=CH_2)_3$, $N(CH_2CH_2OH)_2CH_2CH_2OH$	
		$N(CH_2CH_2OCH=CH_2)_3$	Negative
		$C_6H_5NHCH_2CH_2OCH=CH_2$	"
		$(C_6H_5)_2NCH_2CH_2OCH=CH_2$	"
5	N-Vinyl lactams	$N(CH_2)_n-CO$ / $CH=CH_2$ ($n = 3,4,5$)	Positive
6	Vinyl esters	$CH_2=CH-OCOCH_3$	"
7	Vinyl sulfides	$CH_2=CH-S-C_2H_5$	Negative

$$CH_2=CHX+KOI \rightarrow CH_2ICH(X)(OK) \rightarrow CH_2ICHO+KX \quad (3)$$

in which X = —OR or $-NCO(CH_2)$

In both cases the reaction product is iodoacetaldehyde, which then reacts with iodine and alkali in the usual way. The overall process can be represented by the equation:

$$CH_2=CHX+3I_2+KOH+H_2O \rightarrow CHI_3+3HI+XH+COOK. \quad (4)$$

In Table 1 will be found a list of the vinyl compounds whose behavior in the iodoform reaction was studied. A negative reaction was found for those containing an aromatic nucleus. It is known from the literature [5] that in a number of cases the presence of an aromatic nucleus interferes with the iodoform reaction. The authors explained this phenomenon as the effect of steric factors [5]. It is very probable that

the inertness of vinyl ethers containing a benzene ring is to be explained not only by steric hindrance, but also by the character of the double bond in these compounds.

The iodoform reaction is not given also by vinyl sulfides $CH_2=CHSR$ owing to combination of iodine with the sulfur atom.

Apart from vinyl compounds we have tested some acetals and allied compounds in the iodoform reaction. The substances examined were the symmetrical acetals $CH_3CH(OR)_2$, in which R=CH_3, C_2H_5, C_3H_7-i, C_4H_9, C_8H_8, and the mixed acetals $CH_3CH(OCH_3)OC_4H_9$, $CH_3CH(OC_4H_9)OC_8H_{15}$, $CH_3CH(OC_2H_5)OCH_2CH_2OH$, $CH_3CH(OC_4H_9)OC_8H_4OCH_3$, $CH_3CH(OC_2H_5)OC_8H_{11}$, $CH_3CH(R')NCO$, R' = C_2H_5, C_8H_9.

When a carefully purified acetal was used in the reaction, the result, without exception, was negative: after addition of alkali and iodine the solutions remained quite clear, and no precipitate of iodoform was formed. Hence, the iodoform reaction can be used as a supplementary test in the qualitative analysis of vinyl ethers and N-vinyl lactams, enabling them to be distinguished from, for example, the corresponding acetals.

It was of interest also to determine the possibility of using this reaction for the quantitative determination of the vinyl compounds studied. For N-vinyl lactams only one method is known for their quantitative determination, this being based on their hydrolytic breakdown in an acid medium [6]; on the other hand, numerous papers [7] have been devoted to the quantitative analysis of vinyl ethers. In the present investigation, therefore, attention was directed mainly to the possibility of the use of the iodoform reaction in the analysis of N-vinyl lactams, particularly as these are readily soluble in water and the performance of the analysis does not present any experimental difficulties.

It is well known that the iodoform method is used for the quantitative determination of acetone, one molecule of which requires six atoms of iodine. There is no exact information in the literature of the quantitative determination of acetaldehyde and iodoacetaldehyde by this method—only some isolated conflicting statements [8]. It has been established [9] that the best results are obtained in the determination of acetaldehyde when the following conditions are observed: reaction temperature 25°, duration 25 minutes, mixture of reactants in following order—add weighed sample of substance to be analyzed to alkali solution, and then add the necessary amount of iodine. But even under such conditions, acetaldehyde was accounted for only to the extent of 80%. This behavior results from the simultaneous occurrence of two reactions when the aldehyde is treated with iodine and alkali:

$$CH_3CHO + 6I + 4KOH \rightarrow CHI_3 + 3KI + HCOOK + 3H_2O. \quad (5)$$

$$CH_3CHO + 2I + 3KOH \rightarrow CH_3COOK + 2KI + 2H_2O. \quad (6)$$

Reaction (5) results in the formation of iodoform (6 atoms of iodine are consumed per molecule of acetaldehyde), and reaction (6) consists in the oxidation of aldehyde to acid (2 atoms of iodine are consumed per molecule of acetaldehyde). Thus, for formaldehyde, in which the methyl group is absent and the enol form cannot exist, reaction (6) proceeds quantitatively. Hence, the actual stoichiometric coefficient for the reaction between acetaldehyde, iodine, and alkali varies between 2 and 6.

When the above-stated conditions were verified for N-vinylcaprolactam [2-oxo-1-vinylhexamethyleneimine], it was found that they are indeed optimum. However, as in the case of acetaldehyde, when the results of the analysis were calculated from Formula I (see below) on analogy with acetone and in accordance with Equation 4—the extent to which the vinyl lactam was accounted for was only about 75%.

$$\%VL = \frac{(a-b)\,FM}{p \cdot 6 \cdot 100} \cdot$$

in which a is the amount (ml) of thiosulfate solution required in the control experiment, b is the amount (ml) of thiosulfate solution required in the actual determination, F is the correction factor to 0.1 N thiosulfate, M is the molecular weight of the vinyl lactam under investigation, and p is the weight taken of the vinyl lactam.

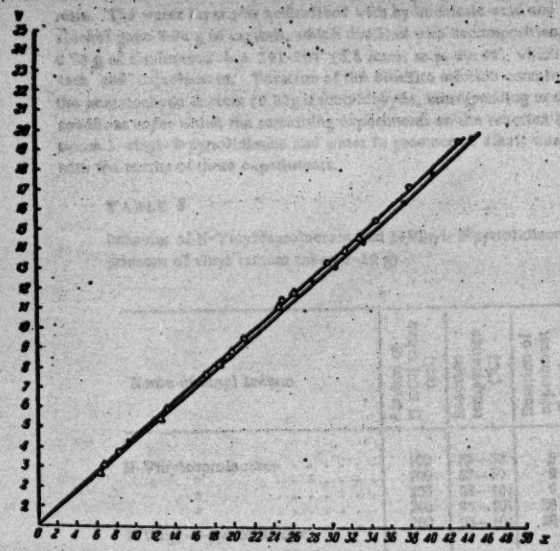
TABLE 2

Experimental Data for the Calculation of the Proportionality Coefficient K.

For 1-vinyl-2-pyrrolidinone					For N-vinylcaprolactam					For 1-vinyl-2-piperidone				
Sample No.	Amount taken for analysis ($\times 10^{-5}$ equiv): $10^5 \cdot x$	Amount (ml) of 0.1 N I_2 used; $10^4 \cdot y$		K (calculated)	Sample No.	Amount taken for analysis ($\times 10^{-5}$ equiv): $10^5 \cdot x$	Amount (ml) of 0.1 N I_2 used; $10^4 \cdot y$		K (calculated)	Sample No.	Amount taken for analysis ($\times 10^{-5}$ equiv): $10^5 \cdot x$	Amount (ml) of 0.1 N I_2 used; $10^4 \cdot y$		K (calculated)
		1st determination	2nd determination				1st determination	2nd determination				1st determination	2nd determination	
1	33.00	14.70	14.55	4.460	1	6.19	2.84	2.84	4.587	1	17.048	7.87	7.87	4.620
1	44.00	20.1	20.1	4.567	1	12.38	5.64	5.64	4.556	1	24.572	11.76	11.76	4.605
1	55.00	25.04	24.88	4.550	1	24.76	11.39	11.39	4.599	1	34.096	15.85	15.83	4.649
2	30.00	13.50	13.32	4.500	1	30.95	14.29	14.19	4.613	1	42.620	19.93	19.93	4.669
2	40.00	18.20	18.20	4.554	2	18.27	8.44	8.44	4.612	1	24.572	11.77	11.75	4.617
3	9.25	4.30	4.30	4.648	2	24.36	11.34	11.34	4.655	1	42.620	19.91	19.95	4.684
3	18.50	8.37	8.50	4.584	3	6.47	3.17	3.02	4.667	2	8.333	3.86	38.8	4.645
3	27.75	12.63	12.60	4.552	3	12.94	5.99	5.99	4.629	2	20.828	9.70	9.70	4.661
3	37.00	16.68	16.78	4.535	3	19.41	8.97	8.97	4.621	2	29.167	13.57	13.59	4.659
3	46.00	21.26	21.41	4.621	3	25.88	12.14	12.09	4.671	2	37.500	17.65	17.65	4.707
						32.35	14.91	14.91	4.609					
Mean				4.58	Mean				4.62	Mean				4.65

It is evident that also in the iodoform determination of vinyl lactams, reactions analogous to (5) and (6) occur (in this case, reaction is with iodoacetaldehyde).

As it was found that in the determination of vinyl lactams very concordant results were always obtained and the analytical procedure was very simple and rapid, we considered that, without undertaking the task of establishing the actual mechanism of the reaction, it would be very desirable to find an empirical formula for the calculation of the analytical results. For this purpose we applied the graphical method, so widely used in analytical chemistry.



Determination of the coefficient K: ●– 1-vinyl-2-pyrrolidinone; ○ – 1-vinyl-2-piperidone; △ – N-vinylcaprolactam.

We obtained a straight line (see Figure), which can be described by the equation $y = Kx$. The proportionality coefficient K is the ratio between the numbers of vinyl lactam molecules and iodine atoms that react together, i.e. in effect the stoichiometric coefficient for the reaction studied (for numerical data see Table 2). The vinyl lactam content of a weighed sample of material can therefore be calculated from Formula II (see Experimental).

For N-vinylcaprolactam K = 4.62, for 1-vinyl-2-piperidone 4.65, and for 1-vinyl-2-pyrrolidinone 4.56. For vinylcaprolactam and vinylpiperidone K can be determined accurate within ± 1%, and for vinylpyrrolidinone accurate within ± 1.5%. The coefficients found are practically all the same.

By the use of Formula II, very satisfactory results were obtained in the quantitative determination of vinyl lactams. Hence, when an error of up to 2-3% is permissible in analysis, the iodoform reaction can be used successfully for the determination of the substances indicated, particularly in aqueous solutions.

EXPERIMENTAL

Reaction of N-Vinylcaprolactam with Water in Presence of Caustic Potash

A mixture of 10.1 g of N-vinylcaprolactam (2-oxo-1-vinylhexamethylenimine) [b.p. 90.5-91° (1.5-2mm), n_D^{20} 1.5130] and 200 ml 1N KOH was prepared in a three-necked flask fitted with stirrer, thermometer, tube for passage of nitrogen, and reflux condenser connected to three Tishchenko vessels. It was heated for 30 hours at 99-101° in a current of nitrogen. The reaction mixture was extracted with four successive 20-ml portions of ether. The ether extracts yielded 5.93 g of vinylcaprolactam [b.p. 91-91.5° (2 mm), n_D^{20} 1.5097] and 0.6 g of resin. The water layer was neutralized with hydrochloric acid and evaporated. Extraction of the residue with alcohol gave 2.64 g of crystals, which distilled with decomposition. Fractional distillation of this product gave 0.25 g of a substance b.p. 101-107° (2.5 mm), m.p. 32-40° which was found to be a mixture of vinylcaprolactam and caprolactam. Titration of the bisulfite solution contained in the Tishchenko absorption vessels gave the acetaldehyde content (0.22 g of acetaldehyde, corresponding to 0.69 g of vinylcaprolactam, was found). The conditons under which the remaining experiments on the reaction between vinylcaprolactam and water and between 1-vinyl-2-pyrrolidinone and water in presence of alkali were carried out are given in Table 3 together with the results of these experiments.

TABLE 3

Behavior of N-Vinylcaprolactam and 1-Vinyl-2-pyrrolidinone Toward Water in Presence of 1N KOH (amount of vinyl lactam taken 9-10 g).

Name of vinyl lactam	Amount of N KOH taken (ml)	Reaction temperature (°C)	Duration of experiment (hours)	Amount of vinyl lactam recovered unchanged (g)	Amount of acetaldehyde found (%)	Resinous products obtained (g)
N-Vinylcaprolactam	100	57—50	5	8.74	—	0.5
"	200	57—50	9	6.45	—	0.98
"	200	98—101	9	4.22	5.77	0.35
"	200	98—101	26	4.78	17.61	1.23
1-Vinyl-2-pyrrolidinone	200	98—101	26	0.37	10.84	3.80

Qualitative Determination of Vinyl Compounds by the Iodoform Method

Experimental Procedure. A test tube containing 2 ml 1N KOH and one drop (0.03-0.05 ml) of the compound under investigation was shaken while 2 ml of 0.1 N iodine was added. A large excess of iodine interferes with the test, since under these conditions the iodoform dissolves. In the presence of the compounds indicated in Table 1, a turbidity appeared and later settled as a precipitate of iodoform with its characteristic odor.

Quantitative Determination of Vinyl Lactams by the Iodoform Method

a) Experimental Determination of the Proportionality Coefficient. A 1.0-g sample of the freshly distilled vinyl lactam was dissolved in 1 liter of distilled water. An exact amount of this solution (10-50 ml, generally measured by buret) and 25 ml 0.1N iodine were added to 25 ml 1 N KOH contained in a flat-bottomed conical flask. The mixture was kept at 23-25° for 25 min; then acidified with 1N HCl (26 ml). The excess of iodine was titrated with thiosulfate. Knowing the amount y of iodine consumed by the amount (g-equiv) of vinyl lactam taken for analysis x, we calculated the value of K (Table 2).

b) Determination of the Concentration of Vinyl Lactam. In the determination of the concentration of vinyl lactam we used the same procedure. The calculation was carried out by Formula II:

$$VL = \frac{(a-b)\cdot Fkl}{p \cdot K \cdot 100} \quad (1)$$

in which K is the empirically found proportionality coefficient.

SUMMARY

1. It was shown that many vinyl compounds (vinyl ethers, N-vinyl lactams) give the iodoform reaction, and this fact can be applied to the qualitative analysis of these compounds.

2. It was shown that vinyl lactams undergo practically no hydrolysis in presence of alkali.

3. A mechanism is proposed for the formation of iodoform by the action of alkali and iodine on the vinyl compounds indicated.

4. A procedure was developed for the quantitative determination of N-vinylcaprolactam, 1-vinyl-2-pyrrolidinone, and 1-vinyl-2-piperidone by the iodoform titration method.

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BRIEF COMMUNICATIONS

USE OF A NICKEL CATALYST IN THE KIZHNER DECOMPOSITION OF HYDRAZONES

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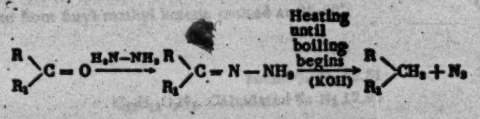
As is well known, in 1911 Kizhner [1] found that aldehydes and ketones can be converted into the corresponding hydrocarbons by catalytic decomposition of their hydrazones:



At first, Kizhner used caustic potash for the decomposition of hydrazones, but later he showed that more complete reaction, with higher yields of the corresponding hydrocarbons, could be obtained by the joint action of caustic potash and platinum.

For the hydrazone-decomposition reaction, Cook and Linstead [2] used palladium instead of platinum. Thus, in the preparation of cis-octahydropentalene they used palladium supported on barium sulfate as catalyst. For similar purposes, Fischer and Krauss [3] successfully used palladium on calcium carbonate.

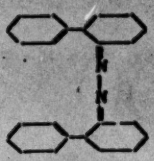
In the present investigation we studied the use of finely divided nickel as catalyst for the Kizhner reaction. With this object we carried out comparative experiments on the decomposition of hydrazones of 2-(1-cyclohexen-1-yl) cyclohexanone and furyl methyl ketone in presence of platinized alumina (20% Pt), reduced nickel-alumina catalyst (30% Ni), and nickel black. We showed that, in the Kizhner reaction, a platinum catalyst can be successfully replaced by a more accessible nickel catalyst.

EXPERIMENTAL

2-(1-Cyclohexen-1-yl) cyclohexanone was prepared by the self-condensation of cyclohexanone in presence of hydrogen chloride and decomposition of the 2-(1-chlorocyclohexyl) cyclohexanone formed by means of 20% caustic potash solution. It had the following properties: b.p. 110° (7 mm); n_D^{20} 1.5073; d_4^{20} 0.9990; Found MR 53.11; Calculated $C_{12}H_{18}O$ MR 52.76.

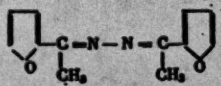
Furyl methyl ketone was prepared by Hartough and Kosak's method [4], which consists in the acetylation of furan by means of acetic anhydride in presence of hydriodic acid. It had b.p. 46-48° (5 mm) and m.p. 31°.

In the preparation of the hydrazones, 90% hydrazine hydrate, taken in 10-20% excess, was added to an ethanolic solution of the ketone; the reaction mixture was then heated in a water bath for 3-4 hours. In addition to the hydrazines, small amounts of azines were obtained in this reaction, and these were isolated when the reaction products were vacuum-distilled: they are yellow crystalline substances, insoluble in water, but readily soluble in alcohol, ether, and benzene. The azine obtained from 2-(1)cyclohexen-1-yl) cyclohexanone melted at 103°:



Found %: N_2 7.85
$C_{26}H_{26}N_2$. Calculated %: N_2 7.94

The azine from furyl methyl ketone melted at 95-96°:



Found %: N_2 13.51
$C_{11}H_{11}O_2N_2$. Calculated %: N_2 12.95

Alcohol was distilled off, and the hydrazones were carefully dried with anhydrous calcium chloride. They were then decomposed with freshly calcined caustic potash (10% on the weight of the hydrazone in presence of catalyst (0.1% of platinized alumina, 0.5% of nickel on alumina, or 2% of nickel black).

Nickel on alumina (30% Ni) was prepared from nickel and aluminum nitrates by the method developed by Shuikin and coworkers [5]. Nickel black was prepared by leaching the aluminum from a nickel-aluminum alloy (27% Ni) with dilute caustic soda solution.

The hydrazones were decomposed in a Claisen flask fitted with condenser set for distillation. It was necessary to initiate reaction by slight warming, after which it went fairly vigorously. It was found that care is necessary to prevent overheating of the reaction mixture, as the liquid may then be thrown over into the receiver. In order to complete the decomposition it is desirable to add a little fresh catalyst toward the end of the operation.

The catalyzates were treated with dilute acetic acid, washed with water, and dried over calcined calcium chloride. When distilled over sodium, 1-cyclohexylcyclohexene came over at 235° (752 mm); it had n_D^{20} 1.4942; d_4^{20} 0.9082; Found MR 52.57; Calculated $C_{12}H_{20}$ MR 52.75.

2-Ethylfuran distilled at 91-91.5° (750 mm) and had n_D^{20} 1.4402; d_4^{20} 0.9018; Found MR 28.11; Calculated C_6H_8O MR 28.42.

The results of the hydrazone-decomposition experiments are given in the table.

TABLE 2

Yields of Hydrocarbon and 2-Ethylfuran (%) in the Decomposition of Hydrazones in Presence of Various Catalysts

Original substance	$Pt-Al_2O_3$	$Ni-Al_2O_3$	Ni black
Hydrazone of 2-(1-cyclohexen-1-yl)cyclohexanone	60.8	58.0	55.0
Hydrazone of furyl methyl ketone	72.0	75.0	69.0

Our experiments have therefore established that nickel deposited on alumina (30% Ni) and nickel black can be used successfully for the decomposition of the hydrazones of 2-(1-cyclohexen-1-yl, cyclohexanone and furyl methyl ketone. Moreover, these experiments show that the hydrazones of ketones of various structures can be decomposed with adequate completeness not only in presence of platinum, but also in present of a nickel catalyst.

SUMMARY

It was shown that, in some cases, various forms of finely dispersed nickel (nickel on alumina and nickel black) can be used instead of a platinum catalyst, and with equal effect, in the hydrazone-decomposition reaction.

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SULFONATION OF TERT-BUTYL-SUBSTITUTED THIOPHENES

Ya. L. Goldfarb, L. V. Antik, and P. A. Konstantinov

It is known that compounds which have aromatic functions and carry a tert-butyl group have certain peculiarities associated with the screening effect of this group. New data have recently appeared in the literature concerning this effect of the tert-butyl group [1-3]. The steric effect of the tert-butyl group is apparent not only in cases when compounds containing this group do not enter this or that reaction, but also in cases in which attempts are made to introduce a tert-butyl group into an aromatic system. Examples of this sort can be found in the work of Schlatter [4]. This investigator found that m-xylene is tert-butylated exclusively in the 5-position, and p-xylene will scarcely undergo tert-butylation. In these and other cases there is a tendency for the tert-butyl group to enter a position that is spatially far removed from other substituted groups. However, the general picture that is obtained on the basis of such facts does not yet enable us to predict the behavior of individual compounds containing a tert-butyl group. Thus, contrary to expectation, no clear distinction could be drawn between 2,5-di-tert-butyl- and 2,5-dimethyl-thiophenes in their desulfurization in presence of Raney nickel. The first of these compounds, like the second, is readily acetylated in presence of stannic chloride and readily undergoes King formylation; on the other hand, 3,5-di-tert-butyl-2-methylthiophene is not formylated and forms an acetyl derivative only as the result of the elimination of one tert-butyl group. In view of these results, it appeared to be of interest to accumulate further facts relating to the properties of tert-butyl-substituted thiophenes, investigating, in particular, their behavior toward sulfonating and nitrating agents.

In the present paper we give the results of a study of the sulfonation of 2,5-di-tert-butylthiophene (I), 3,5-di-tert-butyl-2-methylthiophene (II), and 2-tert-butyl-5-methylthiophene (III). As sulfonating agents we used a solution of sulfur trioxide in dichloroethane and pyridine-bis[sulfur trioxide], which has been extensively applied to the sulfonation of acidophobic systems by Terentyev [5].

The first compound (I), when treated with a solution of SO_3 in dichloroethane (40% excess of SO_3), formed a monosulfonic acid, which we isolated in about 75% yield in the form of the sodium salt. The sulfonation of (I) with pyridine-bis[sulfur trioxide] on dichloroethane gave the same monsulfonic acid. In order to characterize the sulfonic acid, we prepared its acid chloride and p-toluidine salt. It was shown that the acid was 2,5-di-tert-butyl-3-thiophenesulfonic acid, for when hydrolyzed in presence of phosphoric acid it gave the original 2,5-di-tert-butylthiophene, which was brominated to a dibromo derivative identical with the previously described 3,4-dibromo-2,5-di-tert-butylthiophene [6].

When the sulfonation of (I) was carried out in presence of a large excess of SO_3 in dichloroethane solution [5 moles of SO_3 per mole of (I)], one of the tert-butyl groups was eliminated with formation of a tert-butylthiophenedisulfonic acid, in which one of the sulfo groups was evidently in an α-position. The unchanged position of the remaining tert-butyl group was established by the isolation of 2-tert-butylthiophene when the disulfonic acid was hydrolyzed in presence of phosphoric acid. The identity of the tert-butylthiophene was confirmed by the properties of the aldehyde derived from it.

The sulfonation of (II) proceeded in low yield, and one of the tert-butyl groups was eliminated. The position of the remaining tert-butyl group was made clear when (III) was sulfonated. The p-toluidine salts of the two sulfonation products were identical.

It was thus shown that in the sulfonation of (II) the tert-butyl group eliminated was in the β-, not the α-position, the product being 5-tert-butyl-2-methyl-3-thiophenesulfonic acid. Whether the sulfo group entered the ring in the β-position adjacent to methyl or in that adjacent to butyl was not subjected to special investigation, but the former must be considered more probable on the basis of steric considerations.

EXPERIMENTAL

Sulfonation of 2,5-Di-tert-butylthiophene with Pyridine-bis[sulfur trioxide]. A mixture of 2.9 g (0.015 mole) of 2,5-di-tert-butylthiophene, 3.7 g (0.015 mole) of pyridine-bis[sulfur trioxide], and dichloroethane was shaken for 14 hours. The lumps that formed were periodically rubbed out. The mass was treated with 20 ml of water. A glistening precipitate of a complex compound with pyridine was formed, and this was broken down by addition of a concentrated solution containing 6.4 g of sodium carbonate. After one hour, the sodium salt of the sulfonic acid was filtered off (2.7 g). After crystallization from water and vacuum drying over phosphoric oxide at 100° to constant weight, the yield was 2.37 g (about 50%).

Found %: C 45.40; 45.56; H 6.50; 6.55; S 19.98; 19.83 Na 7.67; 7.66
$C_{12}H_{19}O_3S_2Na \cdot H_2O$. Calculated %: C 45.52; H 6.69; S 20.28; Na 7.27

Sulfonation of 2,5-Di-tert-butylthiophene with a Solution of Sulfur Trioxide in Dichloroethane. A mixture of 28.7 g of 2,5-di-tert-butylthiophene and 60 ml of dry dichloroethane was stirred at 18° for 20 minutes while 34 g (about 40% excess) of a dichloroethane solution of sulfur trioxide of about 48% strength in dichloroethane was added. After a further 40 minutes the reaction mixture was poured into 200 g of a mixture of water and ice, and the dichloroethane layer was extracted with 100 ml of water, taken in two portions. The aqueous solutions were combined, and addition of saturated sodium carbonate solution gave 37.4 g of the sodium salt of the sulfonic acid. It was recrystallized from water and dried to constant weight over phosphoric oxide in a vacuum at 100°.

Found %: C 45.7; 45.57; H 6.51; 6.57; S 20.04; 20.33; Na 7.28; 7.36
$C_{12}H_{19}O_3S_2Na \cdot H_2O$. Calculated %: C 45.52; H 6.69; S 20.28; Na 7.27

It was thus found that one molecule of water of crystallization was present in the product dried in a vacuum at 100°. In order to remove it the product was further dried to constant weight over phosphoric oxide in a vacuum at 136-140°.

Found %: S 21.40; 21.31; Na 8.16; 8.03
$C_{12}H_{19}O_3S_2Na$. Calculated %: S 21.47; Na 7.71

The yield of the anhydrous sodium salt of the sulfonic acid was about 32.7 g (75%).

p-Toluidine Salt of 2,5-Di-tert-butyl-3-thiophenesulfonic Acid. This was prepared by mixing an aqueous solution of the sodium sulfonate with a solution of p-toluidine in 2% hydrochloric acid. The yield was 70.2% and it melted at 192-193°. After recrystallization from water it formed colorless needles, m.p. 193-194°.

Found %: N 3.75; 3.71
$C_{19}H_{29}O_3S_2N$. Calculated %: N 3.65

Preparation of 2,5-Di-tert-butyl-3-thiophenesulfonyl Chloride. With water cooling, 1 g sodium 2,5-di-tert-butyl-3-thiophenesulfonate was added to 2 ml of phosphoryl chloride, and then 0.75 g of phosphorus pentachloride was added. The mixture was heated in a water bath for 30 minutes, after which the precipitate present was filtered off and the benzene solution was washed with water and dried over calcined magnesium sulfate. After removal of benzene there remained 0.7 g (about 70%) of the sulfonyl chloride, m.p. 84-89°. After three crystallizations from heptane it melted at 91-92.5°.

Found %: C 48.86; 48.89; H 6.41; 6.39
$C_{12}H_{19}S_2O_2Cl$. Calculated %: C 48.85; H 6.5

Hydrolysis of 2,5-Di-tert-butyl-3-thiophenesulfonic Acid. The sodium salt of 2,5-di-tert-butyl-3-thiophenesulfonic acid, in an amount corresponding to about 5 g of the sulfonic acid, was added to 60 ml of aqueous phosphoric acid (sp.gr. 1.633). The solution was heated to 135-140° and subjected to distillation with steam heated to the same temperature. The distillate was extracted with ether, and the extract was dried over calcined sodium sulfate. When ether was removed the product crystallized. The yield was 2.55 g (about 72%), and the product had m.p. 20-21°, b.p. 115-116° (30 mm), and n_D^{20} 1.4920.

Found %: C 73.59; 73.61; H 10.04; 10.12

$C_{12}H_{22}S$. Calculated %: C 73.40; H 10.265

The resulting di-tert-butylthiophene was brominated under the conditions necessary for the formation of 3,4-dibromo-2,5-di-tert-butylthiophene [6]. The yield of bromination product was almost quantitative. After two crystallizations from alcohol it melted at 62-63.5°. There was no melting point depression in a mixture test with 3,4-dibromo-2,5-di-tert-butylthiophene.

Sulfonation of 2,5-Di-tert-butylthiophene with a Solution of Sulfur Trioxide (in large excess) in Dichloroethane. Over a period of 90 minutes, 400 g of a freshly prepared 50% solution of SO_3 in dichloroethane (2.5 moles SO_3) was added to a cooled stirred solution of 98 g (0.5 mole) of 2,5-di-tert-butylthiophene in 200 ml of dry dichloroethane, the temperature being maintained at 18-20° during the addition and for a further 40 minutes. The reaction mixture was poured on 700 g of ice, and the dichloroethane layer was extracted with three 100-ml portions of water. The aqueous solutions were united. When saturated sodium carbonate solution was added to this solution, the sodium salt of the sulfonic acid was not precipitated. The solution was made weakly acid by addition of sodium carbonate, and the p-toluidine salt of the sulfonic acid was precipitated by the addition of a hydrochloric acid solution of p-toluidine. The product was 121 g (47%) of a substance of m.p. 224-225°. After three crystallizations from water melted at 237-238° (with decomposition).

Found %: C 51.32; 51.29; H 6.06; 5.94; S 18.86; 18.69

$C_{22}H_{32}O_6N_2S_3$. Calculated %: C 51.34 H 5.88; S 18.69

The substance obtained was therefore the di-p-toluidine salt of a mono-tert-butylthiophenedisulfonic acid.

The hydrolysis of the tert-butylthiophenedisulfonic acid was carried out in presence of phosphoric acid under conditions similar to those described above apart from the reaction temperature, which was 180-190°, the steam being superheated to the same temperature. Suitable treatment gave a product of b.p. 162-163° and n_D^{25} 1.4980, which corresponds to 2-tert-butylthiophene. The product was formylated [7], and the aldehyde isolated had b.p. 135-137° (25 mm) and n_D^{25} 1.5468; semicarbazone m.p. 215-216°; oxime m.p. 121-122°*.

Mixture tests on the corresponding derivatives of known 5-tert-butyl-2-thiophenecarboxaldehyde showed no melting point depression.

Sulfonation of 3,5-Di-tert-butyl-2-methylthiophene. Over a period of 5 minutes at 10-12°, 4.35 g (30% excess) of a dichloroethane solution of SO_3 of about 48% strength was added to a stirred solution of 4.24 g (0.02 mole) of 3,5-di-tert-butyl-2-methylthiophene in 10 ml of dry dichloroethane. The reaction mixture was then stirred for a further 40 minutes at 12-18°.

The mixture was washed with several 30-ml portions of water, and the p-toluidine salt was isolated under conditions similar to those described above. The product was 1.6 g of a substance melting at 167-181°. After recrystallization from water there remained 0.93 g (13.6%), m.p. 184.5-185.5°.

Found %: C 56.2; 56.43; H 7.01; 6.81; N 4.36; 4.28

$C_{16}H_{23}O_3NS_2$. Calculated %: C 56.27; H 6.79; N 4.102

It was thus established that the sulfo group displaced one of the tert-butyl groups.

No special investigation was made on the products contained in the dichloroethane layer.

Sulfonation of 2-tert-Butyl-5-methylthiophene. The reaction conditions were as in the preceding experiment, and the sulfonic acid was isolated in the form of its p-toluidine salt, obtained in 61.5% yield. Its melting point was 175-182°, raised to 184-185° by recrystallization from acetone. It gave no melting point depression in admixture with the p-toluidine salt prepared from the sulfonation product from 3,5-di-tert-butyl-2-methylthiophene.

SUMMARY

1. It was shown that when 2,5-di-tert-butylthiophene (I) and 2-tert-butyl-5-methylthiophene (II) were sulfonated with 1.3-1.4 molecular equivalents of sulfur trioxide, the corresponding monosulfonic acids were

* For 5-tert-butyl-2-thiophenecarboxaldehyde the literature [8] gives: oxime m.p. 86°, semicarbazone m.p. 249°.

formed. When (I) was sulfonated with 5 molecular equivalents of sulfur trioxide, one of the tert-butyl groups was eliminated and a disulfonic acid was formed.

2. In the sulfonation of 3,5-di-tert-butyl-2-methylthiophene (II) with 1.3 molecular equivalents of sulfur trioxide, a 5-tert-butyl group was eliminated, and the product was a monosulfonic acid identical with the sulfonation product from (III).

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DIFFERENTIAL TITRATION OF TRIPEPTIDES AND PIPERAZINEDIONES IN THE POLYCONDENSATION PRODUCTS FROM GLYCINE ETHYL ESTER

K. T. Poroshin, T. D. Kozarenko, and Yu. I. Khurgin

In the determination of the amount of piperazinediones in the polycondensation products from glycine esters [1] and alanine esters prepared under various conditions, in a number of cases we have found it impossible to apply the "copper" method [2]. The reason for this, as spectrophotometric investigation showed, was the presence of an appreciable amount of tripeptide esters among the polycondensation products. In this connection, we found it necessary to develop a method for the separate determination of piperazinediones and tripeptides in presence of peptides of greater length.

EXPERIMENTAL

We based our method on a phenomenon that one of us had discovered previously [3]: the successive combination of peptides of different lengths with cupric ions in an alkaline medium with formation of copper "biuret" complexes. It was established that, depending on the length of the peptide, complexes of different characteristic absorption spectrum and different visual color were formed. It was shown that, as copper was added to a solution of a mixture of peptides of different lengths, "red" complexes were first formed with tetrapeptides and peptides having still longer chains (λ_{max} 510-520 mμ). Model experiments showed that "violet" complexes (λ_{max} 530 mμ) with tripeptides were formed only after the complete binding of the longer peptides by copper. Hence, in absence of dipeptides (this case is found at the later stages of the polycondensation reaction of α-amino-acid esters), the determination of the amount of tripeptides consists in measuring the amount of copper entering the complex from the "transition point" to the final end point (appearance of a slight suspension of cupric hydroxide). The transition point is the point at which the binding by copper of tetrapeptides and still longer peptides ends and the binding of tripeptides begins. The transition point can be detected visually by the appearance of a characteristic violet shade. Spectrophotometric checks showed that visual determination of the transition point can be carried out with the necessary accuracy. It is important to note that the method is applicable only to substances soluble in an alkaline medium.

As the titration with copper is carried out in an alkaline medium, it was essential to exclude the possibility of the hydrolysis of piperazinediones. For this reason the titration was carried out at room temperature in 0.1 N NaOH. Under these conditions, the piperazinediones derived from glycine and alanine are not hydrolyzed appreciably during the time required (2-3 minutes) for the titration. A longer titration time is associated with some hydrolysis of piperazinediones. At the same time it is impossible to use weaker alkali solutions for the titration, for the binding of tripeptides and longer peptides by copper is not then complete [3].

At 40° in 0.1 N NaOH, the hydrolysis of piperazinediones proceeds irrespective of the presence of copper complexes of peptides, so that the determination of the piperazinedione content can be done by the copper method in the same test sample. Hence, the procedure for separate, differential titration is as follows: a) dissolution of the test sample in not less than 100 times the amount of 0.1 N NaOH (volume for weight); b) determination of the amount of tripeptides by finding the transition point and end point of the titration with copper (for samples of 5—15 mg it is convenient to use 0.04 N $CuSO_4$); c) hydrolysis of piperazinediones in the same solution for 2-4 hours at 40° and determination of the content of anhydrides from the extra amount of copper bound after hydrolysis. Simultaneously, an alkaline solution of the polycondensation product is hydrolyzed at 40° so that the amount of piperazinediones can be determined by measuring the increase in amino nitrogen [2] by the van Slyke method. From this solution a test is taken for a repeat determination of the transition

point (verification of the stability of peptides during the alkaline hydrolysis of piperazinediones) and the determination of the total amount of copper used in the formation of "biuret" complexes with tri- and di-peptides formed during the hydrolysis of the piperazinediones. Our experiments showed good reproducibility (within ± 5%) of results in the differential titration of polycondensation products from glycine and DL-alanine ethyl esters.

The polycondensation of glycine and DL-alanine ethyl esters was carried out by the procedure described previously [4]. Carbon dioxide, dried over sulfuric acid, was used as catalyst and was added in amounts of 2 and 4 mole-% on the original amount of the ethyl ester of the amino acid. The dosage of the carbon dioxide was accurate within 1.5% of the total amount of catalyst. Reaction was at 40 ± 0.1° for 12 hours. For glycine ethyl ester the extent to which the reaction went to completion was 72% for 2 mole-% of catalyst and 80% for 4 mole-% of catalyst. The resulting polycondensation products were removed from the ampoules [4] and carefully ground three times with ether in order to remove monomer from the solid. After removal of ether in a desiccator over sulfuric acid, the products were investigated. They were readily soluble in water and in weak alkaline and acid solutions. At 160° they became dark-colored, and from 160° to 306° they melted with charring. In the polycondensation product obtained in presence of 2 mole-% of catalyst, 9.8% of tripeptides and 16.9% of piperazinediones were found by titration with copper, and by increase in amine nitrogen 17.9% of piperazinediones was found. When the reaction was carried out in presence of 4 mole-% of catalyst, 17.8% of tripeptides and 10.0% (copper method) or 12.5% (amine method) of piperazinediones were found. The proposed method can be used for investigating the composition of the polycondensation products obtained from esters of α-amino acids at various stages of the reaction.

SUMMARY

1. A method is proposed for the differential titration of polycondensation products of esters of α-amino acids.

2. The amounts of piperazinediones and tripeptides were determined among the products obtained under various conditions by the polycondensation of glycine ethyl ester.

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ADDITION OF CH_3SiHCl_2 AND $C_2H_5SiHCl_2$ TO CHLORO-, CHLOROTRIFLUORO-, AND TETRAFLUORO-ETHYLENES

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Very little study has been devoted to organosilicon compounds containing fluorine in an alkyl or aryl radical. This is associated with the fact that methods for the synthesis of fluoroalkyl- and fluoroaryl-silanes have not yet been adequately developed. Examination of the literature shows that there are the following general methods for the preparation of such compounds: heteroorganic [1-8], direct synthesis [9-11], the Swarts reaction [8], and copolymerization of alkenylsilanes with perfluoroolefins [12].

In a previous investigation [13] we successfully effected the additions of CH_3SiHCl_2 and $C_2H_5SiHCl_2$ to allyl and 2-methylallyl chlorides in presence of platinized charcoal:

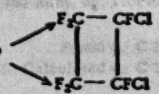
$$CH_3SiHCl_2 + CH_2{=}CHCH_2Cl \rightarrow CH_3Si(Cl)_2CH_2CH_2CH_2Cl.$$

In view of the above mentioned application of this reaction to such fully halogenated olefins as $F_2C{=}CFCl$, and $F_2C{=}CF_2$, we may point out a new simple method for the preparation of organosilicon compounds containing fluorine in the alkyl chain. We must mention, in this connection, that in a patent by Wagner there is a passing reference to the possibility of bringing about the addition of $HSiCl_3$ to $F_2C{=}CH_2$ in presence of platinized charcoal. Also, a study of the direction of the addition of CH_3SiHCl_2 and of $C_2H_5SiHCl_2$ to chloro compounds of the vinyl type, including $CF_2{=}CFCl$, is of undoubted interest.

The addition of methyl- and ethyl-dichlorosilanes to $F_2C{=}CFCl$ was found to be considerably more difficult than the corresponding reaction with allyl chloride. The yield of addition product was 23% on the amount of CH_3SiHCl_2 or $C_2H_5SiHCl_2$ that reacted. The following peculiar features of the reaction should be noted:

1. The reaction differs from the allyl chloride reaction carried out under the same conditions in that Si-attached hydrogen is not replaced by chlorine (formation of CH_3SiCl_3 and $C_2H_5SiCl_3$), neither are the compounds $CH_3Si(Cl)_2CFHCF_2H$ and $C_2H_5Si(Cl)_2CFHCF_2H$, formed.

2. There is an appreciable side reaction in which

$CF_2{=}CFCl$ dimerizes into 

We also carried out the addition of CH_3SiHCl_2 and of $C_2H_5SiHCl_2$ to vinyl chloride. Unlike Wagner [14] in his work on the addition of $HSiCl_3$ to vinyl chloride, we could isolate only 1-chloroethyl compounds, the formation of which can be represented as follows:

$$RSiHCl_2 + ClCH{=}CH_2 \rightarrow RSi(Cl)_2CH(Cl)CH_3,$$

in which R is CH_3 or C_2H_5.

We cannot, however, exclude the possibility of the formation of β-chloroethyl compounds also; in the course of the reaction these may decompose with formation of CH_3SiCl_3 and $C_2H_5SiCl_3$ * (we isolated the latter in appreciable amount). It should be noted that the addition reactions of CH_3SiHCl_2 and of $C_2H_5SiHCl_2$ with vinyl chloride do not differ in principle, in the sense of the occurrence of side reactions [formation of CH_3SiCl_3, $C_2H_5SiCl_3$, $CH_3Si(Cl)_2C_2H_5$, $(C_2H_5)_2SiCl_2$], from the reactions of the same compounds with allyl chloride [13].

The main difference is in the direction of addition: whereas the $RSiCl_2$ residue adds to allyl chloride at the most highly hydrogenated carbon atom, the reverse occurs with vinyl chloride. The proof of this, however, was rendered difficult by the thermal instability of the β-chloro compounds that could possibly be formed. As the addition products formed by CH_3SiHCl_2 and by $C_2H_5SiHCl_2$ with $F_2C{=}CFCl$ have lower boiling points than $CH_3Si(Cl)_2CH(Cl)CH_3$ and $C_2H_5Si(Cl)_2CH(Cl)CH_3$, they must be assigned the structure of α-chloro-compounds, $CH_3Si(Cl)_2CF(Cl)CF_2H$ and $C_2H_5Si(Cl)_2CF(Cl)CF_2H$, since the corresponding β-chloro compounds should have higher boiling points. Under the above-described conditions, CH_3SiHCl_2 and $C_2H_5SiHCl_2$ add also to tetrafluoroethylene.

EXPERIMENTAL

$CH_3Si(Cl)_2CF(Cl)CF_2H$. A mixture of 115 g of dichloromethylsilane, 110 g of $F_2C{=}CFCl$, and 0.3 g of platinized charcoal (1% Pt) was prepared in an autoclave and heated at 160° for 15 hours. At this temperature the pressure rose to 30 atm and then fell to 20 atm. Fractionation of 163 g of the mixture of reaction products through a 35-plate column gave: 1) 93.5 g of unchanged CH_3SiHCl_2, b.p. 40°, 2) 23 g of $F_2C{=}CFCl$, b.p. 57-58° (734 mm), and 3) 10 g (23% on the amount of CH_3SiHCl_2 that reacted) of $CH_3SiH(Cl)_2CF(Cl)CF_2H$: b.p. 124.5° (734 mm); d_4^{20} 1.4211; n_D^{20} 1.4000; found MR 39.49; calculated MR 39.10

Found %: C 16.71; 16.57; H 2.11; 2.06
$C_3H_4Cl_3F_3Si$. Calculated %: C 16.94; H 1.88

Owing to the presence of Si and Cl in the molecule, analysis for fluorine was difficult and somewhat high results were obtained (Found 28.61% F, Calculated 24.63% F).

$C_2H_5Si(Cl)_2CF(Cl)CF_2H$. A mixture of 130 g of dichloroethylsilane, 170 g of $F_2C{=}CFCl$, and 0.3 g of platinized charcoal under an initial pressure of nitrogen of 25 atm was heated at 160° for 15 hours; the maximum pressure at this temperature was 75 atm. The mixture of reaction products (226 g) was twice fractionated through a 35-plate column and gave 1) 52.6 g of $\begin{matrix} F_2C{-}CFCl \\ | \\ F_2C{-}CFCl \end{matrix}$, b.p. 58° (754 mm), 2) 87.2 g of unchanged $C_2H_5SiHCl_2$, b.p. 74.5° (755 mm), 3) 18.4 g (23% on the amount of $C_2H_5SiHCl_2$ that reacted) of $C_2H_5Si(Cl)_2CF(Cl)CF_2H$: b.p. 154° (754 mm), d_4^{20} 1.4170, n_D^{20} 1.4120; found MR 43.11; calculated MR 43.61.

Found %: C 19.69; 19.88; H 2.26; 2.42
$C_4H_4Cl_3F_3Si$. Calculated %: C 19.57; H 2.50

$CH_3Si(Cl)_2CH(Cl)CH_3$. This was prepared from 102 g of CH_3SiHCl_2 and 108 g of $CH_2{=}CHCl$, which were heated in an autoclave for six hours at 150-160° and 25-30 atm in presence of 0.5 g of platinized charcoal. Fractionation of 119 g of product through a 35-plate column gave:

1. 27 g of CH_3SiHCl_2, b. p. 40.5° (747 mm).

* The formation of CH_3SiCl_3 and $C_2H_5SiCl_3$ can be represented also in another way, for example $RSiHCl_2 + ClCH_2CH_2Si(Cl)_2R \rightarrow RSiCl_3 + CH_3CH_2Si(Cl)_2R$.

1. 16.4 g of CH_3SiCl_3: b.p. 35° (747 mm).

3. 12.7 g of $CH_3Si(Cl)_2C_2H_5$: b.p. 100° (747 mm); d_4^{20} 1.0630, n_D^{20} 1.4197; Found MR 34.04; Calculated MR 34.17.

4. 12 g (7%) of $CH_3Si(Cl)_2CH(Cl)CH_3$: b.p. 134° (741 mm); d_4^{20} 1.2170; n_D^{20} 1.4480; Found MR 39.12; Calculated MR 39.01. The literature [15] gives b.p. 136°.

$C_2H_5Si(Cl)_2CH(Cl)CH_3$. This was prepared from 130 g of $C_2H_5SiHCl_2$ and 117 g of CH_3CHCl, which were heated in an autoclave for 14 hours at 160-165° and 25 atm in presence of 0.4 g of platinized charcoal. Two fractionations of 210 g of reaction products through a 35-plate column gave 1) 8.7 g of $C_2H_5SiHCl_2$, b.p. 74-75° (765 mm), 2) 52 g of $C_2H_5SiCl_3$, b.p. 98° (765 mm), 3) 38 g of $(C_2H_5)_2SiCl_2$, b.p. 129.8° (765 mm), 4) 25 g (13%) of $C_2H_5Si(Cl)_2CH(Cl)CH_3$, b.p. 161° (730 mm), d_4^{20} 1.1970, n_D^{20} 1.4575; Found MR 43.62; Calculated MR 43.64. The literature [16] gives b.p. 41.5° (9 mm); d_4^{20} 1.2017, n_D^{20} 1.4578.

$CH_3Si(Cl)_2CF_2CF_2H$. This was prepared under the same conditions. The yield was 13.9 g (15% on the amount of CH_3SiHCl_2 that reacted), and it had b.p. 95.2° (753 mm); d_4^{20} 1.3879; n_D^{20} 1.3689; Found MR 34.95; Calculated MR 34.29.

$C_2H_5Si(Cl)_2CF_2CF_2H$. The yield of this substance was 12.2 g (20% on the amount of $C_2H_5SiHCl_2$ that reacted), and it had b.p. 119.7° (748 mm); d_4^{20} 1.3527; n_D^{20} 1.3819; Found MR 39.40; Calculated MR 38.80.

SUMMARY

1. The addition of CH_3SiHCl_2 and of $C_2H_5SiHCl_2$ to $F_2C=CF_2Cl$, $CH_2=CHCl$ and $F_2C=CF_2$ in presence of platinized charcoal was effected for the first time.

2. An investigation was made into the direction of addition of CH_3SiHCl_2 and of $C_2H_5SiHCl_2$ to $F_2C=CFCl$ and $CH_2=CHCl$ under these conditions.

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REACTIONS OF TRICHLOROSILANE AND DICHLOROMETHYLSILANE WITH BENZENE

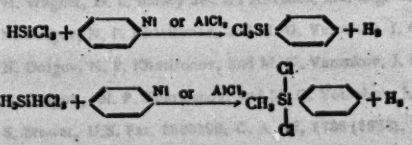
E. A. Chernyshev and A. D. Petrov

A very interesting reaction of silanes containing silicon-attached hydrogen is their addition to unsaturated compounds. This reaction can be initiated by ultraviolet radiation [1], peroxides [1], Friedel-Crafts catalysts [2], platinized charcoal [3], and other agents. Of no less interest is the recently studied reaction of silanes of this type with compounds containing active hydrogen (acids, alcohols, amines, etc. [4-6]). These last reactions proceed with the elimination of hydrogen, for example:

$$R_3SiH + R'OH \rightarrow R_3SiOR' + H_2$$

No papers have been published on the reaction of silanes containing silicon-attached hydrogen with aromatic hydrocarbons, and we are aware only of some short references in patents [7-9] to this reaction.

In the present investigation we have studied the reactions of trichlorosilane $HSiCl_3$ and dichloromethylsilane CH_3SiHCl_2 with benzene. The reactions were carried out in an autoclave at high temperature. In absence of catalyst no reaction was observed between these compounds at temperatures of up to 300°. When palladized or platinized charcoal was used as catalyst (temperature in experiments 270-300°), only traces of reaction products were isolated. Successful results were obtained when Raney nickel and aluminum chloride were used as catalysts. When benzene reacted over Raney nickel with trichlorosilane and with dichloromethylsilane, trichlorophenylsilane and dichloromethylphenylsilane were obtained in yields of 24% and about 18% respectively. With aluminum chloride the yields of trichlorophenylsilane and dichloromethylphenylsilane were 32% and 23% respectively. All of the products were methylated, and the Raman spectra of the resulting trimethylphenylsilanes were determined. The results showed that the products were aromatic silahydrocarbons, not containing any hydrogenated forms as impurity. The reactions, therefore, proceed as follows:



EXPERIMENTAL

1. Reaction of Trichlorosilane with Benzene in Presence of Nickel. A mixture of 268 g of trichlorosilane, 156 g of benzene, and 10 g of Raney nickel was prepared in a one-liter rotating steel autoclave, which was heated at 300° for 12 hours. After the autoclave had cooled, the pressure was 45 atm. Nickel was filtered off, and the reaction product was fractionated through a 30-plate column. The following fractions were collected: Fraction I, $HSiCl_3$, b.p. 31-33° (743 mm), 73.5 g; Fraction II, $SiCl_4$, b.p. 55-57° (734 mm), 51.5 g; Fraction III, C_6H_6, b.p. 79-80° (743 mm), 123.7 g; Fraction IV, 73.4 g of trichlorophenylsilane, b.p. 195-196° (743 mm); n_D^{20} 1.5222; d_4^{20} 1.3144; Found MR 48.74; Calculated MR 48.84. Yield on the amount of trichlorosilane that reacted, 24%.

2. Reaction of Dichloromethylsilane with Benzene in Presence of Nickel. The substances taken were dichloromethylsilane (228 g), benzene (156 g), and nickel (10 g). The reaction conditions were as indicated above. The pressure in the autoclave before unloading was 50 atm. Fractionation gave: Fraction I, CH_3SiHCl_2, b.p. 41-42° (749 mm), 54.3 g; Fraction II, CH_3SiCl_3, b.p. 64.5-65° (749 mm), 53.5 g; Fraction III, $(CH_3)_2SiCl_2$, b.p. 70-71° (749 mm), 18.3 g; Fraction IV, C_6H_6, b.p. 79.5-80.5° (749 mm), 128.5 g; Fraction V, 51.3 g of dichloromethylphenylsilane, b.p. 203.5-204° (749 mm); n_D^{20} 1.5175; d_4^{20} 1.1824; Found MR 48.45; Calculated MR 49.21. Yield on the amount of dichloromethylsilane that reacted, 17.7%. Residue, 6.8 g.

3. Reaction of Trichlorosilane with Benzene in Presence of Aluminum Chloride. A mixture of 268 g of trichlorosilane, 156 g of benzene, and 10 g of aluminum chloride was prepared in a one-liter rotating steel autoclave, which was heated at 300° for 12 hours. After the autoclave had cooled, the pressure was 50 atm. The autoclave was opened, 5 g of sodium chloride was added, and the mixture was heated at 100° for one hour. When the autoclave was cool it was unloaded; the $AlCl_3 \cdot NaCl$ complex was filtered off, and the product was fractionated, the fractions collected being: Fraction I, $HSiCl_3$, b.p. 30-33°, 85 g; Fraction II, $SiCl_4$, b.p. 56-57° (740 mm), 38.4 g; Fraction III, C_6H_6, b.p. 79-80° (740 mm), 125.4 g; Fraction IV, 87.3 g of trichlorophenylsilane, b.p. 195-195.5° (740 mm); n_D^{20} 1.5232; d_4^{20} 1.3148; Found MR 48.81; Calculated MR 48.84. Yield on the amount of trichlorosilane that reacted, 32%. Residue, 8.3 g.

4. Reaction of Dichloromethylsilane with Benzene in Presence of Aluminum Chloride. The substances taken were dichloromethylsilane (228 g), benzene (156 g), and aluminum chloride (10 g). Reaction conditions were as in Experiment 3. Before the addition of sodium chloride the pressure in the autoclave was 55 atm. Fractionation gave: Fraction I, CH_3SiHCl_2, b.p. 41-42° (748 mm), 25.3 g; Fraction II, CH_3SiCl_3, b.p. 65-66° (748 mm), 62.4 g; Fraction III, $(CH_3)_2SiCl_2$, b.p. 70-71° (748 mm), 32.4 g; Fraction IV, C_6H_6, b.p. 79.5-80° (748 mm), 125.3 g; Fraction V, 78.8 g of dichloromethylphenylsilane, b.p. 203-204° (742 mm); n_D^{20} 1.5182; d_4^{20} 1.1832; Found MR 48.68; Calculated MR 49.21. Yield on the amount of dichloromethylsilane that reacted, 23%. Residue, 40 g; this distilled over a wide range of temperature, 120-206° (12 mm).

The spectrum analysis was carried out by Yu. P. Egorov, to whom we express our thanks.

SUMMARY

It was shown that trichlorosilane and dichloromethylsilane react with benzene when heated in presence of nickel or aluminum chloride with formation of hydrogen together with trichlorophenylsilane and dichloromethylphenylsilane, respectively.

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SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 3. REACTION OF PROPYLENE OXIDE WITH ALKYL- AND ARYL-CHLOROSILANES

M. F. Shostakovsky, M. S. Malinovsky, M. K. Romantsevich, and D. A. Kochkin

The reactions between olefin oxides and halogen-containing organosilicon compounds have not received adequate study. The most complete study has been made of the condensations of ethylene oxide [1-3], and, as a result, new oxygen-containing organosilicon compounds have been prepared in accordance with the general scheme:

$$R_nSiCl_{4-n} + (4-n)\ H_2C\!-\!CH_2 \;(O) \longrightarrow R_nSi(OCH_2CH_2Cl)_{4-n}$$

Other epoxides that have been brought into reaction with halogen-containing organosilicon compounds are epichlorohydrin and glycidol [4], which react in accordance with the following equations:

$$R_nSiCl_{4-n} + (4-n)\ H_2C\!-\!CH\cdot CH_2Cl \;(O) \longrightarrow R_nSi(OCH_2CHClCH_2Cl)_{4-n}$$

$$R_nSiCl_{4-n} + (4-n)\ H_2C\!-\!CH\cdot CH_2OH \;(O) \longrightarrow R_nSi(OCH_2CHClCH_2OH)_{4-n},$$

from which it follows that the epoxy ring of these compounds is broken on the side of the primary carbon atom.

With the object of obtaining further information on the position in which the epoxy ring opens, we undertook the present investigation, in which we describe the preparation of (2-chloropropoxy)ethyldichlorosilane, bis(2-chloropropoxy)methylsilane, bis(2-chloropropoxy)dimethylsilane, bis(2-chloropropoxy)ethylsilane, and tris(2-chloropropoxy)vinylsilane from propylene oxide and the corresponding alkylchlorosilanes. Our experiments showed that the α-epoxy ring in propylene oxide is opened on the primary-carbon side. This was confirmed by nitric acid oxidation of the hydrolysis products of the above esters. One of the hydrolysis products was a chloropropanol, which was oxidized to 2-chloropropionic acid, showing that the hydrolysis product was in fact 2-chloro-1-propanol and therefore that the epoxy ring of propylene oxide had opened on the primary-carbon side.

Hence, reaction between propylene oxide and alkyl- and aryl-chlorosilanes can be represented as follows:

$$R_nSiCl_{4-n} + (4-n)\ H_2C\!-\!CH_2\cdot CH_3 \;(O) \longrightarrow R_nSi(OCH_2CHClCH_3)_{4-n}.$$

Formula of product	Organosilicon reactant: Formula	n_D^{20}	d_4^{20}	B.p. in °C (p in mm)	Yield of alkyl(2-chloropropoxy) silane (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Analysis: C_{Si}, % found	C_{Si}, % calculated	H_{Si}, % found	H_{Si}, % calculated	Si, % found	Si, % calculated	Cl, % found	Cl, % calculated
$i\text{-}C_4H_9Si(OCH_2CHClCH_3)_2$ C_4H_9 H	$i\text{-}C_4H_9SiHCl_2$ C_4H_9	1.4350	0.880	138—140	84.9	80—80.5(2)	1.4350	0.9161	59.24	59.35	51.57 51.57	51.77	10.45 10.26	10.56	13.50 13.55	13.45	16.92 16.79	16.89
$CH_3Si(OCH_2CHClCH_3)_2$ H	CH_3SiHCl_2	1.405		41	73.3	85.5—87(3)	1.4391	1.0015	45.36	45.53	36.74 36.78	36.96	8.72 8.66	8.88	12.06 12.06	12.15	31.54 31.10	30.87
$(CH_3)_2Si(OCH_2CHClCH_3)_2$	$(CH_3)_2SiCl_2$	1.4330		70	77.1	72.5—76(3.5)	1.4378	1.0753	59.84	60.00	39.33 39.37	39.16	7.14 7.25	7.30	10.74 10.61	11.45	28.12 28.43	28.88
$C_6H_5Si(OCH_2CHClCH_3)_3$ H	$C_6H_5SiHCl_2$	1.413	1.082	74—77(2)	69.3	85.5—95.5(3)	1.4405	1.0630	60.39	60.36	49.60 49.51	49.15	7.02 7.07	7.40	11.20 11.38	11.45	27.85 28.13	28.58
$H_2C=CHSi(OCH_2CHClCH_3)_3$ H	$H_2C=CHSiHCl_2$	1.395		82.5—84.5 (752)	72.0	103.5—114(2)	1.4371	1.1457	79.34	79.62	39.70 39.54	39.52	6.63 6.71	6.91	8.94	8.97	31.34 31.20	31.68

in which R is alkyl or aryl.

The resulting (2-chloropropoxy) silanes are mobile liquids having a feeble ethereal odor. They can be vacuum-distilled without decomposition. They are soluble in ether, alcohol, and other organic solvents. Some physico-chemical properties of these compounds are given in the table.

EXPERIMENTAL

1. Preparation of (2-Chloropropoxy) ethylisobutylsilane. Propylene oxide (29.04 g, i.e. 0.5 mole) was placed in a three-necked round-bottomed flask fitted with mechanical stirrer, thermometer, dropping funnel, and reflux condenser. Chloroethylisobutylsilane (75.36 g, i.e. 0.5 mole) was added from the dropping funnel at such a rate that the temperature of the reaction mixture did not rise above 30-35°. When the whole of the chlorosilane had been added, the reaction mixture was heated at 35-45° for eight hours and was then set aside overnight at room temperature. Repeated distillation of the reaction products gave 38.6 g (84.9%) of (2-chloropropoxy) ethylisobutylsilane (for constants see table). The other alkyl (2-chloropropoxy) silanes were prepared similarly.

2. Hydrolysis of Bis (2-chloropropoxy)ethylsilane. A mixture of 49.5 g (0.2 mole) of bis (2-chloropropoxy)ethylsilane and 80 ml of nitric acid (sp.gr. 1.4) was prepared in an Erlenmeyer flask. After the mixture had been shaken vigorously, it became warm, copious gas evolution occurred, and a gelatinous precipitate formed. The flask was then warmed in a water bath at 40-50° for one hour in order to complete reaction. In order to remove nitric acid, 250 ml of water and 40 ml of concentrated hydrochloric acid were added. The liquid was separated from the gelati-

hour precipitate and distilled. A fraction of b.p. 184-185° (753 mm) was separated. It corresponded in properties to 2-chloropropionic acid, which would result from the oxidation of 2-chloro-1-propanol. The properties found for the fraction were: b.p. 184-185° (753 mm); d^{20} 1.3858; d_4^{20} 1.379; n_D^{20} 1.4815; MR 22.36; calculated $C_3H_5O_2Cl$ MR 22.41. For $CH_3CHClCOOH$ the literature [5] gives b.p. 185°, d^{20} 1.398.

SUMMARY

1. The reactions between propylene oxide and the following alkylchlorosilanes were investigated: chloroethylisobutylsilane, dichloromethylsilane, dichlorodimethylsilane, dichloroethylsilane, and trichlorovinylsilane.

2. The following compounds were prepared and characterized for the first time: (2-chloropropoxy) ethylisobutylsilane, bis(2-chloropropoxy)methylsilane, bis(2-chloropropoxy)dimethylsilane, bis(2-chloropropoxy)ethylsilane, and tris(2-chloropropoxy)vinylsilane.

3. When propylene oxide reacts with chloro organosilanes, its epoxy ring is broken on the side containing the primary carbon atom.

4. The proposed method may be a general one for the preparation of various alkyl- and aryl-(2-halopropoxy)silanes from propylene oxide and various alkyl- and aryl-chlorosilanes.

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CHRONICLE

HUNGARIAN CHEMICAL CONGRESS

The Second Hungarian Chemical Congress was held in Budapest at the end of November, 1955. It was organized by the Hungarian Chemical Society, which was established 1907 and has about five thousand members. In this work the Society was assisted by the Division of Chemical Sciences of the Academy of Sciences of the Hungarian People's Republic. A delegation from the Academy of Sciences of the USSR took part in the work of the Congress; it consisted of V. I. Spitsyn, Corr. Member Acad. Sci. USSR (leader of delegation), A. F. Kapustinsky, Corr. Member Acad. Sci. USSR, and V. V. Koziov, Doctor Chem. Sci.

The work of the Second Hungarian Chemical Congress began on November 17 in the large conference hall of the Academy of Sciences of the Hungarian People's Republic. The Congress opened with a plenary session, which was addressed by G. Szabo*, Assistant Minister for the Chemical Industry of the Hungarian People's Republic and President of the Hungarian Chemical Society. In discussing the problems facing Hungarian chemists, he stated that the great rise in production in Hungarian industry was quantitative rather than qualitative; it was essential to improve the methods of production, to intensify automation, and to fulfil the chemical requirements of the country more completely. The utilization of coal and petroleum remained the main objectives of chemical industry. In the Second Five-Year Plan, such branches of chemical industry as the manufacture of plastics based on vinyl chloride and of synthetic fibers of the 6- and 6,6-nylon types must be established in the Hungarian People's Republic. The production of synthetic liquid fuel, insecticides, fertilizers, and various pharmaceutical products must also be greatly extended. Apart from the organization of new branches of industry, the existing undertakings must be reorganized and rationalized on a higher technical level. It is necessary to turn attention on the introduction of the complexing method of treating Hungarian bauxites, on the manufacture of valuable aluminum alloys, on anticorrosion measures for metals, etc.

G. Szabo stated that, in the period that had elapsed since the First Hungarian Chemical Congress in 1951, chemistry had made significant progress in Hungary and had made its contribution to the development of industry. The speaker referred to the considerable assistance that Hungarian chemistry had received from the USSR and from all of the People's Democracies.

Academician E. Schulek addressed the assembly on the part played by the Division of Chemical Sciences of the Academy of Sciences of the Hungarian People's Republic in the development of chemistry in Hungary, and the sectional sessions of the Congress then began. These were held simultaneously over a period of four days (November 17, 18, 19, and 20), the sections being: inorganic, analytical, and physical chemistry, organic chemistry, and technology. The Congress was attended by about five hundred Hungarian chemists and by chemists from China, the German Democratic Republic, France, Poland, Czechoslovakia, Rumania, Yugoslavia, the German Federal Republic, and other countries. About fifty papers were presented at the Congress by Hungarian chemists, and nineteen by foreign chemists. Many interesting communications were made by Hungarian chemists.

Academician G. Schay summarized the work carried out since 1949 by his team of workers at the Budapest Technical University and the Academy of Sciences of the Hungarian People's Republic (J. Halasz, F. Nad, D. Szekey, and Szeny Endrenei). In order to elucidate the state of the adsorbed phase and the nature of the

* The spellings of most of the Hungarian names, which appear in the original in Russian transcription, have been checked, but there may be a few errors. – Publisher.

forces acting at interfaces, various new experimental methods were developed, in particular a gravimetic method that enables the adsorption process to be followed autographically in the form of a curve for change in weight against time. This method, in spite of the fact that an analytical balance is used instead of a McBain spring balance, was found to be both simpler and more sensitive than the usual method. Another method proposed uses a floating vessel, the upper part of which contains a dish holding the sorbent, so that the course of the process can be recorded from the extent of immersion of the "float" in accordance with Archimedes' principle. Finally, a dynamic method was developed, this being particularly suitable for the measurement of adsorption rates from a stream. This work enabled these workers to establish a simple formula for calculating the volume of a substance (Vn) necessary for the formation of a unimolecular layer on the surface of the adsorbent, knowing the adsorption volume V and the ratio of the equilibrium pressure to the original pressure p/ po:

$$V_n = V\left(1 - \frac{p}{p_0}\right),$$

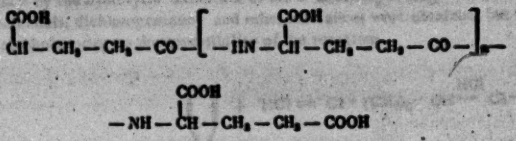
A relationship was established also between the differential heat of adsorption and the heat of evaporation of the sorbate; it was related also to the saturated vapor pressure curve of the sorbate. By the application of the methods of statistical physics, it was shown that the Langmuir adsorption isotherm is not necessarily associated with the localization of adsorption at discrete sites.

Academician E. Schulek (coworkers E. Pungor and J. Trompler) described a newly developed method of titrometric gas analysis. The apparatus that they have designed enables test samples to be taken rapidly and simultaneously from gas and liquid phases with the object of making subsequent microchemical volumetric analyses on these samples. In order to standardize the method, known mixtures of ethanol and methanol were taken. A further study of mixtures of these alcohols with water made it possible to make an analysis of the departures of these systems from Raoult's law. It was suggested that the observed departures of these actual systems from the ideal laws for solutions are to be explained by the chemical peculiarities of the structure of the liquid phases.

Academician L. Erley, in conjunction with his coworkers of the Budapest Technical University, E. Banyai, D. Rady, and E. Zalay, read several papers on the synthesis and applications of several redox indicators of the Variamine blue type. They have prepared new derivatives of Variamine blue with sulfanilide, sulfanisidide, etc., and they have prepared also nucleus-substituted Variamines. A study of their oxidation processes, in which simultaneous measurements of the redox potential were made, enabled them to establish the mechanism of these reactions and its dependence on pH. The authors have successfully applied an acetic acid solution of ascorbic acid for redox titrations, and have in this way determined elementary bromine, bivalent mercury, quadrivalent lead, sexavalent chromium, etc.

Academician A. Buzagh (Budapest Scientific University) read a paper on the effect of freezing on the properties of colloids. In the freezing and subsequent thawing of sols, either there is no change, or coagulation occurs. When coagulation occurs, it may be reversible or irreversible, depending on the experimental conditions (nature and concentration of the sol, rate and degree of cooling). The character of the coagulation depends on the agglomeration of particles and on adhesion phenomena. In this connection the speaker pointed out the applicability of the Ostwald-Buzagh theory of continuity in cases in which the stability of the sol changes after being frozen. Under certain conditions, the freezing of gels promotes peptization, and in some cases it also brings about disaggregation. The speaker explained this phenomenon by the formation of a lyosphere in the colloidal particles. On the basis of the experimental data he examined the effect of water contained in the gel on the peptization process.

Some interesting papers were presented on organic chemistry. Academician V. Bruckner and J. Kovacs (Budapest Scientific University) described their results on the synthesis of the polypeptide γ-poly-a-glutamic acid (molecular weight 9000):



For the synthesis of a polyglutamic acid having α- and γ-glutamic links, the latter predominating, the authors' method of α-ω transpeptidation was used, the substances being converted into their copper complexes to avoid racemization. The substance synthesized corresponded in properties to natural α-polyglutamic acid isolated from the culture medium of Bac. Subtilis (Bac. anthracis).

L. Mester (Budapest Technical University) gave a report on his work on new nitrogen-containing sugar derivatives, (formazans of sugars, phenylhydrazides of thioaldonic acids, etc.). The formazan reaction, which was discovered in 1951 by the author and another Hungarian chemist, G. Zemplén, consists in the treatment of a carbohydrate first with phenilhydrazine and then with aniline diazotized in pyridine; it is widely used, both for simple carbohydrates, and also for the periodic acid oxidation products of various polysaccharides (cellulose, dextrin, insulin, etc.). The formazans obtained were separated by paper chromatography. In many cases the phenylhydrazones were proved to have the aldehyde structure. Only aldehyde phenylhydrazones with an open chain take part in this reaction; ketoses do not form formazans.

L. Vargha (Budapest Pharmacy Research Institute) reported on the synthesis of new carbohydrate derivatives having a cytostatic action. Carbohydrate derivatives containing ethylenimino, 2-chloroethylenimino, and bis-(2-chloroethyl)amino groups were studied. The following compounds were synthesized: 6-deoxy-6-ethylenimino-1,2-isopropylidene-α-glucofuranose ($C_{11}H_{19}O_5N$, m.p. 131-132°), 1,6-dideoxy-1,6-bisethylenimino-3,4--isopropylidene-D-mannitol ($C_{13}H_{24}O_4N_2$), 1,6-bis(2-chloroethylamino)-1,6-dideoxy-D-mannitol dihydrochloride ($C_{18}H_{22}O_4N_2Cl_4 \cdot 2HCl$, m.p. 240-241°), 2-chloroethyl)-D-gluconamide ($C_8H_{17}O_6NCl$, m.p. 144-145°), 2-chloroethylamide of D-glucosaccharic acid ($C_{16}H_{18}O_6N_2Cl_2$, m.p. 172-174°), and others. It was shown that some of these substances have a marked cytostatic action and are of interest as effective anti-cancer agents.

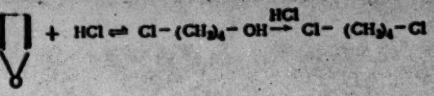
J. Kiss (Sopron Forestry Institute) described the results of investigations on the stereochemistry of amino alcohols and, in particular, of sphingosine, which may be isolated from the nerve tissues of animals. He synthesized sphingosine from the D-erythro-1-amino-2,3-dihydroxylactone of butyric acid; it was found to be identical with the natural product, which has the structure D-erythro-2-amino-trans-4-octadene-1,3-diol. It was established that in natural sphingolactosides such as phrenosine and kerasine the galactose is bound in the α-positions. The author synthesized also 2n-phrenosine and 2n-kerasine, identical with the products isolated from natural sphingolactosides, by the reduction of nervone and oxynervone.

The papers presented at the technological section of the Congress concerned the technology of fertilizers, the treatment of Hungarian bauxites, the electrolytic precipitation of gallium from solutions obtained by the treatment of the bauxites, calculations on continuous columns for the partial oxidation of methane, preparation of high-quality lubrication oils, etc.

Considerable interest was shown in the paper of D. Turzo and L. Kovacs (Synthetic Fibers Research Institute, Budapest) on the preparation of vinyl chloride from gases formed by the partial oxidation of methane. Working independently of the work of Linn and Kobe, which was published in 1954, and working also under different conditions, they used a gas mixture of the composition: C_2H_2 – 8%; H_2 – 53%; CO – 25%; CH_4 – 3%; CO_2 – 2%; HCl – 9%. On the catalyst selected, which worked for more than 300 hours without being in the slightest degree poisoned, there was a 99-100% conversion of acetylene into vinyl chloride.

Academician G. Fodor (Szeged University), in conjunction with L. Berögy and F. Kallai (Organic Chemistry Research Institute, Budapest), presented a paper on the progress made by Hungarian chemists in the chemistry of furan. The main lines of work have been: 1) hydrogenation of 2-furaldehyde at atmospheric pressure over a modified Adkins catalyst with formation of furfuryl alcohol, methylfuran, and tetrahydromethylfuran; 2) oxida-

tion of 2-furaldehyde to 2-furoic acid and the conversion of the latter into furan; 3) preparation of aliphatic compounds by the hydrolytic oxidation of the 2-furaldehyde ring - thus chlorobutanol, dichlorobutane, chloropentanols, dichloropentane, and other substances were obtained, but it was found difficult to prepare chloro alcohols owing to the reversibility of the reaction:



Academician M. Freund, J. Batory, and M. Erdi (Veszprem Petroleum and Gas Institute) reported on the method of deparaffination of petroleum products by extractive crystallization of the urea derivatives. In addition to normal paraffins, components having naphthene and aromatic character are also separated. In the treatment of light, predominantly paraffin, distillates, these are diluted with 4-methyl-2-pentanone, and the urea derivative is obtained with the aid of saturated aqueous urea. The adduct is also decomposed with aqueous urea. In the separation of ceresin it is desirable to use solid urea in presence of an acetone wetter. The method has been checked under industrial conditions.

The members of the Soviet delegation read papers at the appropriate sections of the Congress. V. I. Spitsyn, Corr. Member Acad. Sci. USSR, gave a paper on "The Application of Labeled Atoms in the Investigation of the Chemistry of Complex Compounds", A. F. Kapustinsky, Corr. Member Acad. Sci. USSR, read a paper on "The Thermal Capacity of Ions in Aqueous Solution", and V. V. Kozlov, Doctor Chem. Sci., read a paper on "The Photosensitivity of Selenium-containing Nitro Compounds".

The participation in the Congress was extremely active. As a rule, the presentation of the papers was followed by a lively informal discussion. At the end of the Congress there was a short plenary session at which some concluding remarks were made by the Vice-President of the Hungarian Chemical Society, Academician G. Fodor.

The papers given by the Hungarian chemists showed that chemical research work is carried out in Hungary in a considerable number of scientific institutes and at a high scientific level. Many modern methods of investigation (various physical and physicochemical methods of analysis, thermogravimetry, paper chromatography, microchemical methods, spectroscopic and X-ray structure investigations) are used in these researches. However, radioactive and stable isotopes are scarcely used, the use of infrared spectroscopy is not extensive, and there are no investigations on electron microscopy and electron diffraction.

The investigations of Hungarian chemists are to a considerable degree concentrated on processes for the treatment of natural native raw material (coal, bauxite, petroleum). In these fields they have made great progress during the last five years. It is necessary to take account of the fact that Hungarian research laboratories were almost completely out of action during the war. They have now been reestablished, and many new scientific institutes have been built. The large number of young participants was notable at the Congress (almost one-third of the total number). Many young Hungarian specialist chemists have been trained recently, some of them in the USSR.

From observation of the work of the Congress it may be concluded that Hungarian scientists have adequate contacts with the scientists of other countries, as is evident from the large number of papers given by foreign delegates at the Congress.

Owing to the shortness of our visit to Hungary, our delegation could examine only a few of the scientific establishments. In Budapest we visited various departments (institutes, as they call them in Hungary) of the Etvös Scientific University (which corresponds to our university), the Technical University (which corresponds to our higher technical school), and the Institute of Organic Technology of the Ministry of Chemical Industry. In Veszprem we visited the Chemical University and Petroleum and Gas Research Institute. In Szeged we visited some departments of the chemistry school of the university. The delegation also visited the Tungsram works in Budapest, and there saw the manufacture of the rare metals tungsten and molybdenum and of various electrotechnical and radiotechnical goods.

The laboratories that we examined in the higher educational establishments of Hungary impressed us favorably with respect to the working space, the amount and quality of the equipment, and the number and qualifications of the teachers. It should be noted that the Hungarian higher educational establishments, particularly those in Budapest, were almost completely out of action during the war. They have now been reestablished on a present-day scientific and technical level and on a very much greater scale than in the prewar period.

We must mention also a characteristic feature of the training of chemist in Hungary: the general chemical educations of pure chemists and of applied chemists do not differ essentially in their scope. Specialization begins only from the ninth term, and technologists and chemists trained in Hungary have therefore a very broad general basis of knowledge. The training of a technologist or chemist is generally completed by scientific work for a diploma.

Much scientific research work is carried out in the higher educational establishments that we visited. The quality of this research is in accordance with the highest requirements of modern science; it is carried out with equipment manufactured in Hungary, the USSR, Czechoslovakia, and other countries. The departments are well staffed and have plenty of laboratory space. For the purposes of illustration we may take the Department of Inorganic Chemistry of Budapest University, which is directed by Professor J. Prost: there are 23 teachers and a staff of 35 altogether, including mechanics and glassblowers; the effective working space in the department is 1400 sq.m. (14 laboratory rooms) for a total of only 180 chemical students. It is noteworthy that in Veszprem Chemical University there is a separate building for pilot-scale trials on chemical processes. Such favorable conditions are promising for the future of the development of chemistry in Hungary.

We will now give a brief indication of the lines of work going on in the Hungarian chemical institutes with which we were able to acquaint ourselves. These, of course, are only a few of the Hungarian laboratories in which chemical investigations are being carried out.

The Department of General Chemistry at the Etvös Scientific University (Budapest) is directed by Professor B. Lendiel. Inorganic glasses are being studied in this department from the point of view of their use for the construction of glass electrodes (dependence of the electrochemical properties of the glasses on their compositions, the conditions under which they were prepared, etc.). Another line of work is the synthesis of biuret complexes of metals and the determination of their physicochemical constants. Investigations are being carried out also in connection with the establishment of a silicone industry in Hungary. In particular, the following reaction, which is of interest for the preparation of silicones, is being studied:

$$SiCl_4 + CH_3AlCl_2 \longrightarrow AlCl_3 + CH_3SiCl_3.$$

The Department of Analytical Chemistry is directed by Academician E. Schulek, who is working on the application of physicochemical methods in chemical analysis. The Department of Physical Chemistry is directed by Academician T. Erdey-Gruz. In collaboration with Academician G. Schay, he has written a textbook in two volumes for scientific and technical universities which covers the course in physical chemistry, taking into account the most recent developments. Research on electrochemisty is being carried out in the department (study of overvoltage and other matters related to the mechanism of electrode processes). The Department of the Chemistry and Technology of Colloids is directed by Academician A. Buzagh. For some years now he has been studying phenomena associated with the formation and breakdown of colloid systems and the extension of the practical application of colloid chemistry. The Department of Organic Chemistry of the Scientific University is directed by Academician V. Bruckner, who is studying the structure of natural polypeptides and developing methods for their synthesis.

In the Budapest Technical University, the Department of Inorganic Chemistry is directed by Professor J. Prost, who is carrying out investigations in electrochemistry (polarography, coulometric analysis, electroendosmosis, electrochemical kinetics of coarsely dispersed systems); he has perfected a technique of polarographic analysis. In this department studies are being made also of methods for preparing silicones, and a physicochemical investigation is being made into the behavior of binary mixtures.

The Department of General and Analytical Chemistry is directed by Academician L. Erdey, who is a specialist in inorganic and analytical chemistry and is carrying out investigations along various lines. He has designed an interesting apparatus for thermogravimetry and developed original methods of fluorescence titration. He is studying new indicators for redox titrations.

In the Budapest Technical University there is a combined department of physical chemistry and physics, which is directed by Academician G. Schay. Investigations are going on here on the mechanism of physical adsorption. The techniques of infrared and Raman spectroscopy, as applied to the determination of the structure of chemical compounds, are in the process of being introduced and assimilated. The Department of Organic Chemistry is directed by Professor G. Zemplen. Investigations are being carried out here on natural glycosides. Methods for their synthesis are being developed, particularly for glucosides of the benzalcoumarone group. Nitrogen-containing carbohydrate derivatives are being studied, particularly formazan derivatives. Professor D. Becke is working on the synthesis of physiologically active substances, for example adrenalin, and on the establishment of the structures of alkaloids, in particular cotarnine.

A large center of chemical research in Hungary is the Chemistry School of Szeged University. The Department of Inorganic and Analytical Chemistry is directed by Professor Z. Szabo, who is conducting several lines of investigation: kinetics of gas reactions, namely, the first stages in the oxidation of hydrocarbons; catalytic methods in analytical chemistry; and the use of complex compounds in analytical chemistry. Recently, an investigation of reactions with the aid of magnetic methods has begun. Z. Szabo is interested also in questions associated with the relationship of the properties of elements with their positions in the periodic system.

The Department of Organic Chemistry is directed by Academician G. Fodor. The scientific work of the department is concentrated on the stereochemistry of organic compounds (stereochemistry of nitrogenous compounds, tropine alkaloids, piperidine ring, chloramphenicol, etc.). An investigation on the hydrogenation of furan and processes of oxidizing -furaldehyde is being carried out. Studies of the configurations of carbohydrate derivatives are being carried out with the aid of stereospecific reactions, e.g. $\omega \rightarrow \alpha$ acyl migration, ring closure of 2-ureido and 3-ureido alcohols, formation of lactone salts for proving the configuration of tertiary amino alcohols. At present syntheses of optically active tertiary amines are being carried out; in particular, of 6-tropen-3-ols. In this connection a new method has been developed for the preparation of monoacyl derivatives of diols by the reduction of phenylurethans of hydroxy ketones and the thermolysis of the acylated diol monourethans.

In the Department of Pharmaceutical Chemistry (directed by Professor E. Vinkler) various organic sulfur compounds are being investigated, in particular the reactions of aromatic sulfonyl chlorides (reduction and condensation). The Department of General and Physical Chemistry is directed by Professor A. Kiss. The main lines of investigation are: the mechanism of light absorption, particularly by complex compounds; an electrochemical investigation of the initial stages of the corrosion of metals; and the kinetics of some reactions in solutions.

Much research is being carried out in the laboratories of the Veszprem Chemical University. This establishment corresponds to our institutes of chemistry and technology. The Department of General and Inorganic Chemistry is directed by E. Bodor. Investigations are being carried out on the chemistry of organometallic compounds, namely, metal carbonyl compounds, particularly mixed compounds (cobalt-mercury and others). The polarographic method is used for the determination of germanium and the study of the properties of organometallic compounds. The Department of Inorganic Technology is directed by Professor K. Polinszky, who is a specialist on mineral technology.

The Petroleum and Gas Research Institute (directed by Academician M. Freund), which is also in Veszprem, is carrying out investigations on the deparaffination of lubricating oil distillates by the urea method. Work is being developed also on the oxo synthesis, in which carbon monoxide and cobalt carbonyl are being used (J. Berty). A pilot-scale apparatus has been constructed for the catalytic preparation of acetic acid from methanol at high pressure with iodine as promoter and water as solvent.

Valuable chemical investigations are being carried out in Debrecen University (Professor Szarvas and others), the Pharmaceutical Chemistry Research Institute in Budapest (L. Vargha, J. Kollonitsch, and others), the laboratories of the Sopron Forestry Institute (J. Kiss), the Plant Protection Research Institute in Budapest (K. Szabo), the Synthetic Fibers Research Institute in Budapest (R. Bacskay), and other scientific establishments.

In conclusion we must refer to the exceptionally cordial, warm reception accorded the delegation of the Academy of Sciences of the USSR by the Hungarian Chemical Society and Hungarian scientists. The Hungarian chemists unanimously expressed their desire to strengthen their scientific relations with Soviet chemists and to become acquainted more closely with Soviet experience in science and to make more extensive use of it.

V. I. Spytsin, Corresponding Member
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PHASE DIAGRAM OF THE TERNARY SYSTEM $CaO - BaO - SiO_2$

N. A Toropov, F. Ya. Galakhov, and I. A. Bondar

We have previously studied the solid solutions formed between calcium and barium orthosilicates in a binary orthosilicate system [1]. It was of great interest to investigate the crystallization of these solid solutions in a ternary system; it was necessary to determine the position of the region of separation into layers in the zone of the system rich in silica. Moreover, a study of the system $CaO - BaO - SiO_2$ should aid in the development of new formulations of high refractory ceramics and cements of high density.

Rankin and Wright [2] made a detailed study of the binary system $CaO - SiO_2$, in which they established the existence of four chemical compounds: $CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$. The system $BaO - SiO_2$ was investigated by Eskola [3], and it was established that four compounds were formed in the system: $2BaO \cdot SiO_2$, $BaO \cdot SiO_2$, $2BaO \cdot 3SiO_2$ and $BaO \cdot 2SiO_2$, of which two – barium disilicate and dibarium trisilicate – formed a continuous series of solid solutions. For the ternary system $CaO-BaO-SiO_2$ only a few binary sections have been investigated. Thus, Eskola [3] investigated the section between calcium and barium metasilicates; he finds that a ternary compound $2CaO \cdot BaO \cdot 3SiO_2$ is formed and that this melts at 1320° into $CaO \cdot SiO_2$ and liquid.

Separation into layers in some binary and ternary systems was investigated by Greig [4], who determined the equilibrium temperature for a system of two liquids (glasses) and cristobalite in several binary systems. Olshansky [5] determined the critical layer-formation temperatures in the systems $CaO-SiO_2$ (2110°), $MgO-SiO_2$ (2200°), and $SrO-SiO_2$ (1900°).

EXPERIMENTAL

The samples were prepared from the following materials: 1) silica in the form of a fine powder prepared from rock crystal (99.90% SiO_2); 2) barium carbonate (98.80% $BaCO_3$); 3) calcium carbonate (99.88% $CaCO_3$). A detailed description of the method of preparing the samples and the furnaces used is given in the paper of Toropov, Galakhov, and Bondar [6].

Methods of Investigation

In the study of the phase equilibria of this system we used the quenching method. When the crystallization of a melt was very rapid and a glass could not be obtained, we had recourse to the method of growing large crystals. The sample was weighed in a microfurnace on a loop of molybdenum wire; all the changes occurring in it could be observed through an optical pyrometer provided with a lens giving a high magnification. The temperature was raised until melting was complete, and was then lowered slowly until crystallization began, this point being marked by the appearance of turbidity in the sample. The sample was kept at this temperature for 5-10 seconds and was then thrown from the hot zone of the furnace by means of a magnet. The crystals of the primary phase formed under such conditions differ from the crystals that separate during quenching. The temperature at which crystallization began was determined by reading the temperature at which either the disappearance of crystals or their appearance from the melt could be observed with the aid of the optical pyrometer. When the character of the crystallization was such that it was impossible to determine the temperature at which it began, a simple melting point determination was carried out. The pyrometer scale was calibrated by means of substances of known melting point (calcium aluminate $CaO \cdot Al_2O_3$, 1600°; corundum, 2050°). The establishment of the primary phase and the liquidus temperature was carried out as follows for samples of high silica content: a small fragment of the sample was heated in a graphite crucible in a microfurnace until a definite temperature was reached, at which it was kept for not longer than five minutes. Quenching was effected by throwing the

crucible containing the sample into some Wood's metal by means of a magnet. For samples having high CaO and BaO contents, and also for certain high-silica compositions, cooling was carried out in the furnace without special quenching. Test samples were investigated with the aid of the polarization microscope (immersion preparations and thin sections) and the metallographic microscope (end sections); in some cases x-ray analysis was carried out. The refractive indices of the glasses were determined by the immersion method.

Results of Investigation

Region of layer-separation. As our previous investigation [5] showed, in the binary system $CaO-SiO_2$ the region of layer-separation extends over the composition: 72.0-99.5% SiO_2, and according to our results it extends in the ternary system as far as 11% BaO. This region is demarcated on the diagram (Fig. 1) by a binodal curve

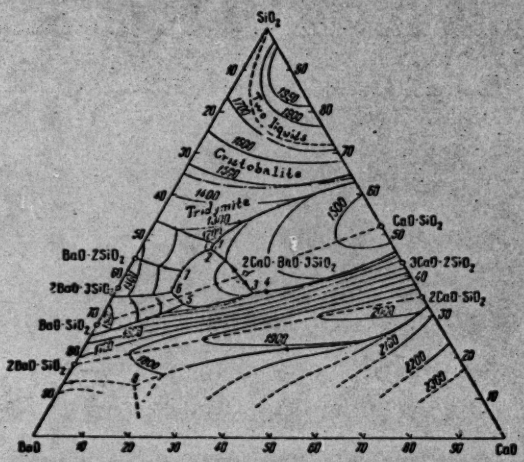

Fig. 1. Region of layer-separation, demarcated on the phase diagram of the system $CaO-BaO-SiO_2$ by a binodal curve (broken line).

(broken line). In the region of layer-separation, two glasses are formed. One glass is more acid (siliceous) and of higher viscosity, and it therefore remains transparent after quenching. The other glass is more basic and fluid, and it is difficult to quench it without the formation of fine crystals within it. x-Ray investigation showed that these fine crystals are grains of cristobalite. Under the microscope samples from the region of layer-separation appear as very small spheres of basic glass distributed through the acid glass. The smallest spheres of basic glass were quenched into transparent ones, but the larger spheres contained separations of cristobalite. In the photomicrographs shown in Fig. 2, a and b, it is possible to see the transparent segregations of basic glass and basic glass containing grains of cristobalite.

As is well known, when one solid and two liquid phases are formed in a binary system, the equilibrium will be invariant, i.e. both temperature and concentration must be constant for the existence of three phases in equilibrium. In this case – for a condensed system – in accordance with the Phase Rule, the number of degrees of freedom must be zero; the equilibrium of three phases will be represented by a horizontal straight line. For ternary systems, equilibrium between one solid and two liquid phases will be represented by a plane. This plane for the existence of three phases will not be horizontal, but will be inclined, owing to the fact that equilibrium in a ternary system is univariant. According to the Phase Rule, there is here one degree of freedom, i.e. the temperature can be changed without disturbing the equilibrium of the system.

We showed that in the system $CaO-BaO-SiO_2$ the plane for the existence of two liquids (glasses) and cristobalite has only a very slight inclination from the binary system $CaO-SiO_2$, in which the temperature for

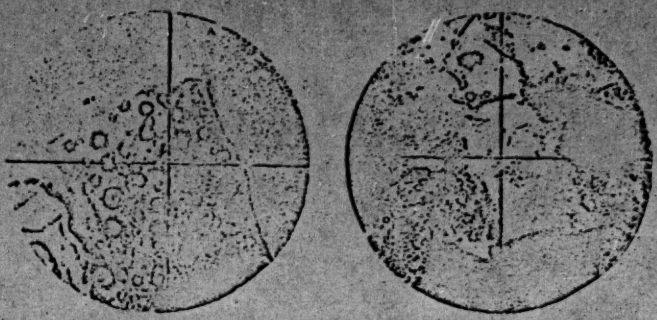

Fig. 2. Photomicrographs showing the formation of two glasses (separation of a basic glass from an acidic glass): a) composition of sample 95% SiO_2, 2.5% BaO, 2.5% CaO; b) composition of sample 90% SiO_2, 5% BaO, 5% CaO. (Transmitted light; × 320)

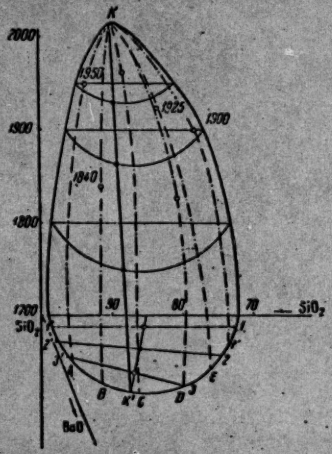

Fig. 3. Space model of layer-separation region in the system CaO–BaO–SiO_2.

the equilibrium of three phases corresponds to 1698°, to the ternary system, in which for 11% BaO the temperature is 1690°. The position of the connode in the region of layer-separation was determined from the refractive indices of acid glasses quenched from 1710°, 1800°, 1900°. If for two different samples the refractive indices of the acid glasses are the same for the same temperature, then the figurative points of these samples are on the same connode; the same applies to the basic glass. Only the proportions of the acid and basic glasses will vary, and these will be related by the law of the lever. Table 1 gives the compositions of samples distributed on eight connodes and the refractive indices of the acid glasses.

In the region of layer-separation, the critical separation temperatures were determined, i.e. the temperatures above which a single glass is formed. The values of the critical separation temperatures for different compositions are given in Table 2.

On the basis of the results of our investigation, a schematic space model of the layer-separation region was constructed (Fig. 3), temperature (°C) being plotted along one axis, and chemical composition (% by weight) along the other two. The model has the form of a dome, at the base of which lies a plane for the coexistence of two liquids (glasses) and one crystalline phase, and the summit of which lies at the critical separation temperature for the binary system CaO–SiO_2 (K). The position of the point K' on the binodal curve was established by Alekseev's law [7]. The coordinates of this point correspond to 5% CaO, 11% BaO, and 84% SiO_2 and a temperature of 1690°.

It follows from Esin's work [8] that the reason for the formation of a layer-separation region lies in the differences in the energies of interaction of ions in silicate melts. This energy of interaction depends on the radius and charge of the metal cation and also on the electronic structures of the ions. If in the dissolution of MO in SiO_2 the interaction forces between the cation and O^{2-} are weaker than the interaction forces between Si^{4+} and O^{2-}, then all of the oxygen ions will move from MO to SiO_2 and separation into layers will not occur. This

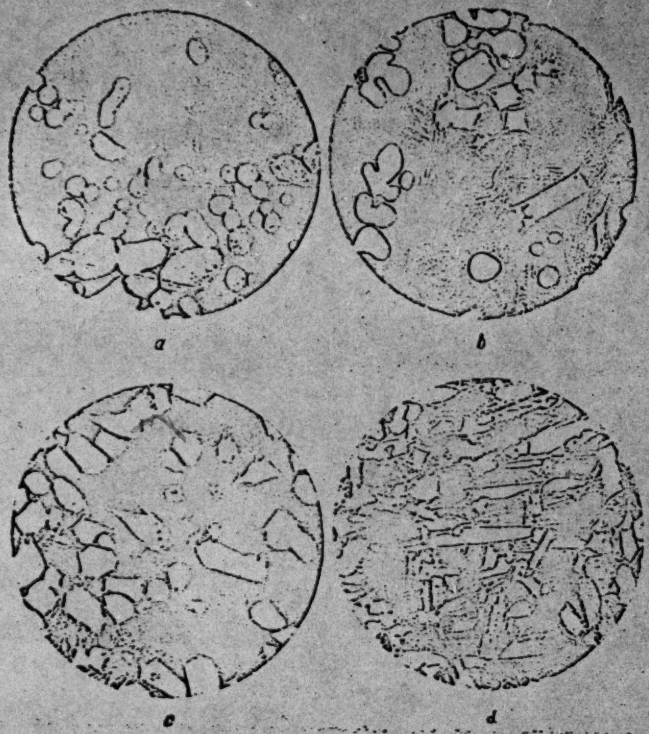

Fig. 4. Photomicrographs showing a series of crystallizations for a composition lying in the solid-solution field close to the $3CaO \cdot 2SiO_2$ field: a) solid solution, 1390°; b) solid solution + $3CaO \cdot 2SiO_2$, 1385°; c) $3CaO \cdot 2SiO_2$, 1375°; d) $3CaO \cdot 2SiO_2 + CaO \cdot SiO_2$, 1360°. (Reflected light; x 420)

phenomenon can be observed when the charge of the cation is less than that of O^{2-} ($Li^+ - 0.78$ A; $Na^+ - 0.98$ A; $K^+ - 1.33$ A) and the radius is greater ($Pb^+ - 1.82$A). Separation into layers is again not observed in the silicates of beryllium ($Be^{2+} - 0.34$A), aluminum ($Al^{3+} - 0.57$A), and boron ($B^{3+} - 0.24$A) owing to the closeness of the interaction forces of these elements and silicon with respect to oxygen. In this case SiO_2 and MO can replace one another and form common groups with oxygen. When there is strong interaction between the cation and oxygen, as found in the silicates of Mg ($Mg^{2+} - 0.78$A), Fe($Fe^{2+} - 0.83$A), Zn($Zn^{2+} - 0.83$A), Mn($Mn^{2+} - 0.91$A), Co($Co^{2+} - 0.78$A), Ni($Ni^{2+} - 0.78$A), Ca($Ca^{2+} - 1.06$A), and Sr($Sr^{2+} - 1.27$A), only a few of the oxygen ions pass over to the SiO_2, the bulk of them surrounding the cation, forming cybotactic groups of different compositions (close to MO and SiO_2). The liquid then becomes microheterogeneous and separates into layers.

As indicated above, in the binary system $CaO - SiO_2$ the region of layer-formation extends within wide limits. Depending on the nature of the cation of a third component that may be introduced, this region may extend insignificantly or may extend further within fairly wide limits in the ternary system. Thus, "weak" alkali-metal cations, cations of high atomic radius (Pb), and also small multivalent cations (Be, Al, B) bring about an insignificant extension of the limits for layer-separation in the ternary system $MO - CaO - SiO_2$. A

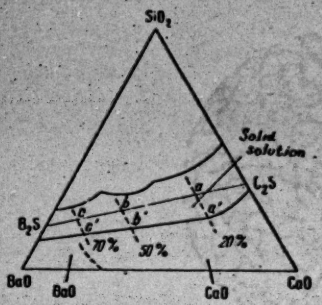

Fig. 5. The positions of sections for the study of the solid-solution field in the ternary system CaO–BaO–SiO_2.

considerable extension of the layer-formation region in the CaO–SiO_2 system is observed when "strong" cations (Mg, Fe, Zn, etc.) – with atomic radii somewhat less than the atomic radius of O^{2-} (O^{2-} – 1.32A) – are introduced. In such ternary systems (MO–CaO–SiO_2), as Greig showed [4], the layer-separation region extends continuously from the CaO–SiO_2 side of the triangle to the MO–SiO_2. A special position is occupied by the Ba ion (Ba^{2+} – 1.43A). Being a strong ion, it has an ionic radius less than that of Pb but greater than those of the above-indicated bivalent cations. Hence, the interaction forces of Ba^{2+} with oxygen will be greater than those of Pb^{2+}, but less than those of Ca^{2+}, Mg^{2+}, and Sr^{2+}. Whereas in the binary system PbO–SiO_2 no region of layer-separation is formed, and in the systems CaO–SiO_2 and MgO–SiO_2 there are considerable layer-separation regions, in the system BaO–SiO_2 there is only a tendency for layer-separation to occur. No clearly defined microheterogeneous regions occur. Our investigation has shown that, when BaO is introduced into the system CaO–SiO_2, a considerable layer-separation region is formed, but this region, demarcated by the binodal curve in Fig. 1, does not reach the BaO–SiO_2 side of the triangle, as is characteristic for the addition of, for example, MgO, when the layer-separation region extends continuously from one side of the triangle (CaO–SiO_2) to the other (MgO–SiO_2).

The $3CaO \cdot 2SiO_2$ Field. Tricalcium disilicate melts at 1475° with decomposition into calcium orthosilicate and liquid. In the binary system CaO–SiO_2 the liquidus line for tricalcium disilicate has a range of only 1% – from 54.5% CaO to 55.5% CaO. In presence of barium oxide, $3CaO \cdot 2SiO_2$ melts with decomposition into a solid solution of calcium and barium orthosilicates and liquid. Hence, the figurative point for the composition $3CaO \cdot 2SiO_2$ lies outside its primary-crystallization field. The $3CaO \cdot SiO_2$ field occupies a very narrow strip, stretching almost to the center of the triangle in the ternary diagram; it borders on fields of calcium metasilicate and solid solutions. In spite of the very narrow width of the field, it was found to be possible to define its position fairly accurately. Table 3 gives the results of the determination of crystalline phases for compositions in the neighborhood of $3CaO \cdot 2SiO_2$.

In samples from the calcium metasilicate field, the secondary phase was tricalcium disilicate, and in no test sample was a solid solution found. When, however, a composition from the solid-solution field was crystallized, the grains of solid solution that formed in the first place disappeared as the temperature fell, and tricalcium disilicate appeared. This course of the crystallization can be seen in the photomicrographs of Fig. 4, which show the crystalline phases obtained by the quenching of test samples of a given composition, 42% CaO, 20% BaO, and 38% SiO_2; the figurative point of this composition lies in the solid-solution field.

Field of Solid Solutions of Orthosilicates, Calcium Oxide, and Barium Oxide

The boundaries between the fields of solid solutions and of the compounds $BaO \cdot SiO_2$, $2CaO \cdot BaO \cdot 2SiO_2$, $3CaO \cdot SiO_2$ were established by the quenching method. In the study of the remaining sections of these fields, the methods of crystal growing and determination of the beginning of crystallization and melting – as described above – were used. Fig. 5 shows the positions of three sections studied, which have constant barium oxide contents of 20%, 50%, and 70%. The inclination of the fusion curves obtained are in accord with data of microscopic analysis for the determination of the primary phases. The points for the maxima a, b, and c, lie on the connecting line of the components of the solid solution; the points for the minima a', b', and c' are on the boundary between the solid-solution field and the calcium oxide field.

The photomicrograph in Fig. 6a shows a solid solution forming large grains of irregular form. Calcium oxide in Fig. 6b appears as small, mainly round grains, sometimes forming clusters. When etched for a short time with water vapor, the calcium oxide grains acquire yellowish and bluish shades. Finally, barium oxide (Fig. 6 c) does not give regular crystals, giving continuous grayish formations, probably owing to its extremely rapid hydration.

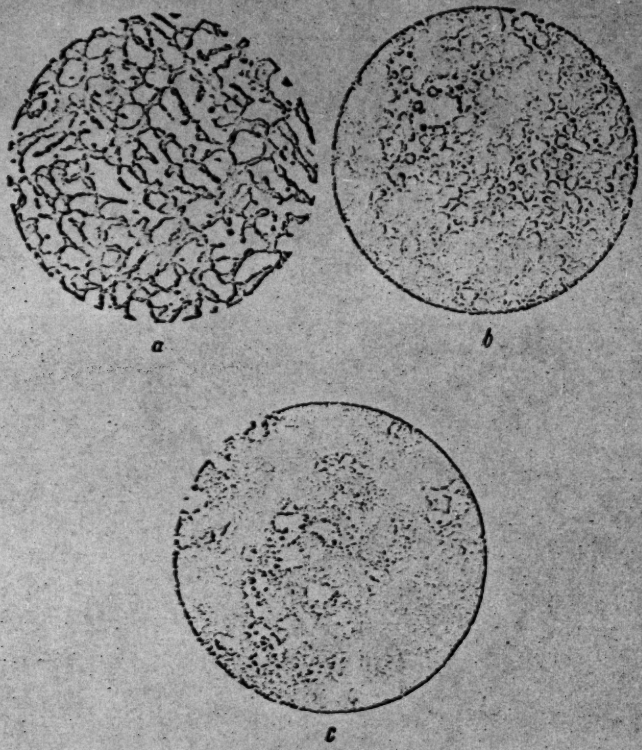

Fig. 6. Photomicrographs: a) solid solution; b) calcium oxide; c) barium oxide. (Reflected light; ×420)

Ternary Diagram of $CaO - BaO - SiO_2$

The fields of stability of crystalline phases, apart from those discussed above, were studied by the usual quenching method. The phase diagram of the system $CaO-BaO-SiO_2$ with plotted isotherms is given in Fig.1. The diagram consists of 12 stability fields for the following phases: I – layer-separation region; II – cristobalite; III – tridymite; IV – calcium metasilicate ($CaO \cdot SiO_2$); V – tricalcium disilicate ($3CaO \cdot 2SiO_2$); VI – solid solutions of barium and calcium orthosilicates; VII – calcium oxide (CaO); VIII – barium oxide (BaO); IX – barium metasilicate ($BaO \cdot SiO_2$); X – solid solutions $2BaO \cdot 3SiO_2$–$BaO \cdot SiO_2$; XI – barium disilicate ($BaO \cdot 2SiO_2$); and XII – the ternary compound $2CaO \cdot BaO \cdot SiO_2$. Eight invariant points were established in the system, six being eutectics and two reaction points. Table 4 gives the compositions and temperatures of the invariant points. The division of the diagram into phase triangles is shown in Fig. 7. The course of the crystallization within the limits of each of these triangles can be established by known methods.

TABLE 1

Refractive Indices of Acid Glasses Quenched from 1710°, 1800°, and 1900° (compositions on the same connode are bracketed together)

No.	Overall composition of sample (% by weight)			Temperature (°C)	Refractive index of the acid glass
	CaO	BaO	SiO_2		
1	23	2	75	1710	1,536
2	8	2	90	1710	1,534
3	18	7	75	1710	1,520
4	10	5	85	1710	1,516
5	10	10	80	1710	1,517
6	7	8	85	1710	1,515
7	23	2	75	1800	1,540
8	8	2	90	1800	1,537
9	14	6	80	1800	1,522
10	10	5	85	1800	1,519
11	10	10	80	1800	1,520
12	7	8	85	1800	1,518
13	18	2	80	1900	1,543
14	14	6	80	1900	1,525

TABLE 2

Critical Separation Temperatures

No.	Composition of sample (% by weight)			Critical separation temperature (°C)
	CaO	BaO	SiO_2	
1	10	—	90	2110*
2	5	5	90	1950
3	5	10	85	1840
4	10	5	85	1965
5	15	5	80	1925
6	20	5	75	1900
7	15	10	75	1825

* According to Ya. I. Olshansky's results [5].

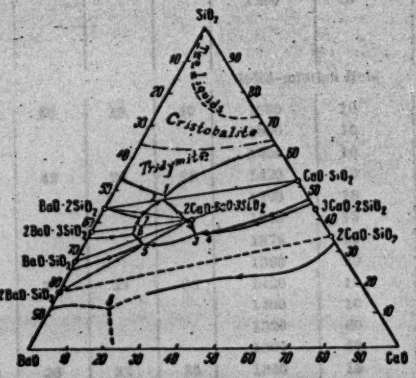

Fig. 7. Phase triangles on the phase diagram of the system CaO – BaO–SiO_2. BaO + $2SiO_2$–SiO_2–CaO · SiO_2; BaO · $2SiO_2$–CaO · SiO_2 – 2CaO · BaO · $3SiO_2$; 2BaO · $3SiO_2$–BaO · $2SiO_2$–2CaO · BaO · 3 SiO_2; BaO · SiO_2; –2BaO · $3SiO_2$ · 2CaO · BaO + $3SiO_2$; BaO–SiO_2; –2BaO · SiO_2 – 2CaO · BaO · $3SiO_2$

TABLE 3

Results of the Determination of the Crystalline Phases in Quenched Samples in the Neighborhood of the $3CaO \cdot 2SiO_2$ Field

Sample No.	Composition of sample (% by weight)			Temperature (°C)	Time held at temperature (minutes)	Phase	Notes
	CaO	BaO	SiO_2				
				$CaO \cdot SiO_2$ field			
205	47	10	43	1480	10	Glass	
				1470	10	Glass + CS	
				1450	10	Glass + CS + C_3S_2	
204	47	13	42	1440	10	Glass	
				1420	10	Glass + CS	
				1380	10	Glass + CS + C_3S_2	
206	48	10	42	1450	10	Glass	
				1445	10	Glass + CS	
				1440	10	Glass + CS + C_3S_2	
48	40	20	40	1400	10	Glass	
				1350	10	Glass + CS	
				1320	10	Glass + CS + C_3S_2	
263	41	20	39	1400	15	Glass	
				1390	15	Glass + CS + C_3S_2	
163	32	32	36	1305	20	Glass	
				1290	20	Glass + CS + C_3S_2	Lies at the boundary with the C_3S_2 field
				Solid-solution field			
56	50	10	40	1600	10	Glass	
				1580	10	Glass + solid solution	
				1400	10	Glass + C_3S_2 + CS (little)	
197	42	20	38	1420	10	Glass	
				1390	15	Glass + solid solution	
				1385	15	Glass + solid solution + C_3S_2	
				1375	20	Glass + C_3S_2	
				1360	20	Glass + C_3S_2 + CS	
162	37	27	36	1420	10	Glass	
				1400	10	Glass + solid solution	
				1320	60	Glass + solid solution + C_3S_2	
				1300	60	Glass + C_3S_2 + CS (little)	
213	33	32	35	1360	15	Glass	
				1340	15	Glass + solid solution	
				1300	60	Glass + solid solution	
				1280	15	Glass + solid solution + C_3S_2	
18	35	30	35	1440	10	Glass	
				1400	10	Glass + solid solution	
				1310	10	Glass + solid solution	
				1280	10	Glass + solid solution + C_3S_2	
155	45	15	40	1430	10	Glass	Lies in the C_3S_2 field
				1400	10	Glass + C_3S_2	
				1380	10	Glass + C_3S_2 + CS	

TABLE 4

Invariant Points of the System $CaO-BaO-SiO_2$

Point	Phases	Process	Composition (% by weight)			Temperature (°C)
			CaO	BaO	SiO_2	
1	$BaO \cdot 2SiO_2$ + $CaO \cdot SiO_2$ + liquid	Eutectic	14.5	38.0	47.5	1160
2	$BaO \cdot 2SiO_2$ + $CaO \cdot SiO_2$ + $2CaO \cdot BaO \cdot 3SiO_2$ + liquid	"	14.0	39.5	46.5	1190
3	$2CaO \cdot BaO \cdot 3SiO_2$ + $CaO \cdot SiO_2$ + solid solution + liquid	Reaction	29.5	34.5	36.0	1300
4	$CaO \cdot SiO_2$ + $3CaO \cdot 2SiO_2$ + solid solution + liquid	"	31.0	33.0	36.0	1310
5	$BaO \cdot SiO_2$ + $2CaO \cdot BaO \cdot 3SiO_2$ + solid solution + liquid	Eutectic	15.5	51.5	33.0	1255
6	$2BaO \cdot 3SiO_2$ + $2CaO \cdot BaO \cdot 3SiO_2$ + $BaO \cdot SiO_2$ + liquid	"	11.5	52.5	36.0	1235
7	$BaO \cdot 2SiO_2$ + $2CaO \cdot BaO \cdot 3SiO_2$ + $2BaO \cdot 3SiO_2$ + liquid	"	11.0	48.0	41.0	1210
8	Solid solution + BaO + CaO + liquid	"	15.0	72.0	13.0	—

SUMMARY

1. On the basis of study of the ternary system $CaO-BaO-SiO_2$ its phase diagram was constructed.

2. The phase diagram consists of twelve stability fields of different phases.

3. The compositions and temperatures at the invariant points were determined.

4. The limits and liquidus temperatures were determined for the field of solid solutions of orthosilicates.

5. The limits of the region of layer-separation and its upper critical point were established, as also was the temperature for the coexistence of a crystalline phase (SiO_2) and two liquids.

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THE DENSITIES OF AQUEOUS URANYL NITRATE SOLUTIONS, AND THE APPARENT MOLAR VOLUMES OF URANYL NITRATE

A. F. Kapustinsky and I. I. Lipilina

The densities of aqueous uranyl nitrate solutions have been the subject of several investigations. Vasilyev [1] examined 18 concentrations over the range 2.8-54.8% by weight at 17°. The results of the remaining authors refer to a very limited number of solutions of various compositions. Thus, Bromer [2] studied two concentrations at 19°. Grant, Darch, Bowden, and Jolines [3] investigated six concentrations over the range 5-25%; this work differs from the remainder in that the densities of the solutions were determined over a wide temperature range (0-100° in steps of 5-20°). Seven dilute solutions (0.4-3.8%) were studied by Gomez [4] at 25°. Some density determinations on uranyl nitrate solutions are reported by de Coninck [5], but these data are rendered valueless by the fact that de Coninck did not state the formula of his salt and the atomic weight assumed for uranium, it being pointed out by Vasilyev [6] that in some of his investigations de Coninck incorrectly assumed that the atomic weight of uranium is 120. The results of Germann [7] are not sufficiently accurate; the third decimal place is found by graphical interpolation.

Although, as will be seen, uranyl nitrate solutions have been investigated by many chemists, not a single investigation has been made in which the densities of these solutions have been studied over the widest possible range of concentrations at a standard temperature (25°) with an accuracy that ensures the possibility of calculating partial molar quantities, i.e. with a probable error of the order of 0.01%. It was with the object of filling this gap that we undertook the present investigation, which finally enabled us to determine the apparent molar volume of the uranyl ion in an aqueous medium.

EXPERIMENTAL

We determined the densities of the solutions pycnometrically. We used a pycnometer of the type employed in one of the most accurate methods of determining densities of solutions – the method of paired quartz pycnometers [8] – but we used only one such pycnometer, thus appreciably simplifying and speeding up the measurements while maintaining adequate accuracy.

The pycnometer (Fig. 1 a), which was constructed of clear fused quartz, had a volume of 38 ml and a weight of 23 g; the internal diameter of the capillary was 1.7 mm. The pycnometer was closed with a quartz cap, ground to fit. One side of the neck of the pycnometer – the side from which measurements were made – was made flat in order to eliminate errors due to refraction. The filling of the pycnometer with water or solution was carried out with the aid of a funnel having a capillary end (Fig. 1b); before being filled, the pycnometer was dried for 48 hours at 130°. Filling, although slow (15-20 minutes) was not difficult; removal of air through the capillary neck of the pycnometer proceeded smoothly. We therefore did not use any supplementary apparatus for, for example, filling in a vacuum or applying excess pressure above the funnel. For the removal of liquid from the pycnometer we used a bent glass tube, one end of which was drawn out into a capillary (Fig. 1c). The liquid was poured out through the capillary neck of the pycnometer and air entered simultaneously through the capillary tube. The pycnometer had one horizontal calibration mark on the neck.

The graduation of the pycnometer, i.e. the determination of the volume it contained when filled up to a level lying within ± 3 cm of the mark on the neck, was carried out with water. In the graduation, the pycnometer was filled with water up to a certain level and immersed in a thermostat, in which it was kept until the level of

the miniscus in the capillary neck of the pycnometer ceased to change. The distance of the meniscus from the mark was determined accurate within 0,01 mm with the aid of a Fmos cathetometer. Thermal equilibrium was generally attained within 20–30 minutes after immersion of the pycnometer in the thermostat. When the meniscus had taken up a constant position, this was read and the pycnometer was closed with the cap. It was then dried with filter paper, allowed to attain the temperature of the analytical balance, and weighed on this balance accurate within one unit in the fifth place of decimals. The correction for weighing in air was made by means of formula:

$$d = d' + 0{,}0012\,(1 - d'),$$

in which d' is the density uncorrected to vacuum-weighing conditions. In the calculation of the volume of water in the pycnometer, the density of water at 25° was taken to be 0,99707 [9]. The results of the graduation of the pycnometer are given in Table 1.

In the determination of the density of a solution, the pycnometer was filled and immersed in the thermostat. When thermal equilibrium had been established and the meniscus had ceased to move in the capillary, the distance from the level of the solution in the capillary to the mark was determined with the cathetometer. The volume of the solution was found by interpolation between the volumes at two closely situated graduated levels, it being assumed that over this distance the cross-sectional area of the capillary was constant.

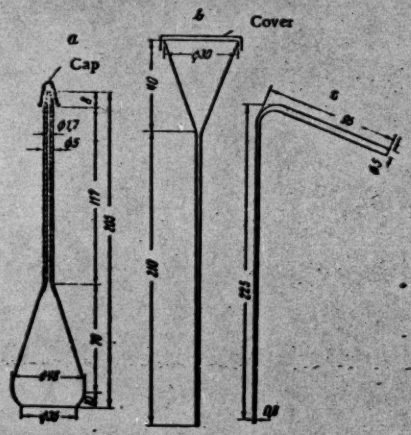

Fig. 1. a) quartz pycnometer; b) funnel for filling; c) tube to assist emptying. (Dimensions shown in mm)

At the end of an experiment the solution was poured out of the pycnometer, which was then rinsed out two or three times with dilute (1:1) nitric acid and ten times with hot water, after which it was dried for two days in a cupboard at 130°. The funnel and bent capillary tube were washed and dried with equal care.

A diagram of the thermostat used for the determination of densities of solutions is shown in Fig. 2. The metal thermostat 1 has the dimensions 430 × 430 × 240 mm; its volume is about 45 liters. Two sides of the thermostat was made of plate glass, so that observations can be made on the apparatus contained in the thermostat. The electric heater 2 consists of nichrome wire wound on a glass frame. The use of the powerful propeller stirrer 3 and the specially constructed large mercury-toluene thermoregulator 4 enables the temperature to be maintained constant within ± 0,002°. All operations are carried out at 25°. The temperature is recorded on the Beckmann thermometer 5, the mercury level in which was established by means of the standard thermometer 6. The pycnometer 7 is held in a clamp so that it is immersed in the water almost up to the cap. During an

TABLE 1

Graduation of the Pycnometer at 25°

Experiment No.	Distance from meniscus to mark (mm)	Weight (g)			Volume of water in pycnometer (ml)
		of dry pycnometer	of pycnometer and water	of water in pycnometer	
1	−27,88	23,34245	61,40551	38,06306	38,17491
2	−12,09	23,34245	61,43913	38,09668	38,20863
3	− 0,52	23,34245	61,47011	38,12766	38,23970
4	+ 3,72	23,34245	61,47434	38,13189	38,24394
5	+11,26	23,34245	61,48926	38,14681	38,25890
6	+24,15	23,34245	61,51885	38,17640	38,28858

experiment the outside of the pycnometer is sometimes covered with small air bubbles which make it difficult to take readings and retard the establishment of thermal equilibrium. These are therefore quickly removed with a thin glass rod covered at one end with rubber tubing; during the experiment this rod is kept in the thermostat and is at 25°. The Beckmann thermometer is read with the aid of a cathetometer, readings being taken every 30 seconds in the preliminary period, i.e. while the pycnometer is being held in the thermostat, and every 2-3 minutes during the main period, when the meniscus is under observation. The temperature is read on the Beckmann thermometer before each reading of the meniscus is taken. Readings of the height of the meniscus and of the calibration mark on the pycnometer are taken every 2 minutes over a period of 30-40 seconds and are accurate within ± 0.01 mm. The probable error in the determination of densities of solutions is 0.001%.

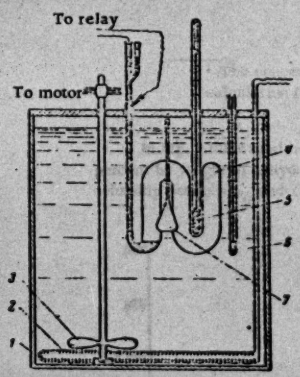

Fig. 2. Diagram of thermostat for the determination of the density of solutions.

The uranyl nitrate was prepared by dissolving UO_3 (chemically pure grade) in chemically pure redistilled nitric acid. The salt so formed was recrystallized three times from water; in the last recrystallization the middle third of the crystals was taken [10]. This salt was dissolved in water so as to give the most concentrated of the solutions to be studied; it had 52.36 % of $UO_2(NO_3)_2$. In the preparation of more dilute solutions the water added and the original solution were weighed, and the concentration of the solution prepared in this way was determined by calculation. In addition, for a series of the solutions, two parallel gravimetric analyses for uranium were also carried out, a weighed amount of the solution being evaporated down in a platinum crucible and the residue calcined to U_3O_8 at 870-890° (the analyzed solutions are indicated by an asterisk in Table 2). The analysis was accurate within 0.01%.

The preparative and analytical part of the work was carried out with water that had been distilled three times in a quartz apparatus, all parts of which were connected through ground glass joints. The conductivity of the purified water was $8 \cdot 10^{-7} - 1 \cdot 10^{-6}$ ohm^{-1}cm^{-1}.

The results obtained for the density d_4^{25} of aqueous uranyl nitrate solutions are presented in Table 2. The same table gives the results of the calculation of V_4^{25}, i.e. the specific volumes of the solutions at 25° referred to the specific volume of water at 4°, and of the apparent molar volumes φ_V, which were found from the formula:

$$\varphi_V = \frac{V_4^{25}(mM + 1000) - (1000/d_w)}{m}. \qquad (1)$$

in which m is the molal concentration of the solution, M is the molecular weight of the salt (394.086), and d_w is the density of water at 25° (0.99707).

TABLE 2

Densities, Specific Volumes, and Apparent Molar Volumes of Aqueous Uranyl Nitrate Solutions at 25°

Experiment No.	Concentration		Density d_4^{25} (g/ml)	Specific volume v_{25} (ml/g)	Apparent molar volume φ_V (ml/mole)	$\sqrt{m}$
	p (% by weight)	molal m				
1*	0,735	0,01871	1,00316	0,99685	67,35	0,137
2*	1,520	0,03916	1,00978	0,99031	67,78	0,195
3*	2,316	0,06016	1,01670	0,98357	65,65	0,245
4*	3,466	0,09111	1,02656	0,97413	67,67	0,302
5	5,880	0,15853	1,04811	0,95410	67,92	0,398
6*	9,020	0,25158	1,07739	0,92817	68,58	0,502
7*	12,05	0,34766	1,10736	0,90315	68,56	0,590
8	15,20	0,45484	1,14002	0,87718	69,19	0,674
9*	18,63	0,58098	1,17739	0,84934	70,33	0,762
10*	21,99	0,71529	1,21751	0,82135	69,81	0,846
11*	24,92	0,84223	1,25370	0,79764	70,58	0,918
12	27,75	0,97462	1,29067	0,77479	71,24	0,987
13	30,57	1,1172	1,33016	0,75179	71,47	1,057
14	33,53	1,2800	1,37439	0,72764	71,67	1,131
15	36,58	1,4636	1,42221	0,70313	72,25	1,210
16	39,19	1,6353	1,46609	0,68209	72,60	1,279
17	43,42	1,9473	1,54389	0,64771	72,83	1,396
18	46,37	2,1931	1,60237	0,62408	73,19	1,481
19	49,38	2,4753	1,66453	0,60077	74,28	1,574
20*	52,36	2,7889	1,73082	0,57776	75,23	1,670

* The concentration of the solution was determined by chemical analysis and by calculation (from weights of original solutions and of added water).

In Fig. 3 the experimental results are presented graphically as a function of concentration, expressed as percent by weight of anhydrous salt. The last column of Table 2 gives values of $\sqrt{m}$, and Fig. 4 gives the relationship between φ_V and $\sqrt{m}$ for aqueous uranyl nitrate solutions. It will be seen that this relationship is linear.

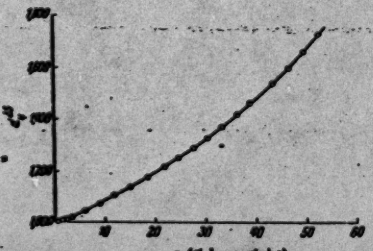

Fig. 3. Densities of aqueous uranyl nitrate solutions at 25°.

As already pointed out, there are data in the literature on the densities of aqueous uranyl nitrate solutions. So that a comparison might be made between our results and the data in the literature, we submitted the latter to the following treatment. As different authors expressed the concentrations of the solutions differently, we recalculated them: in all cases we calculated the molality and percentage by weight (i.e. the amount of anhydrous salt (g) in 100 g of solution) of the solutions; then, from the density data we calculated the specific volumes of the solutions, and hence the apparent molar volumes of the salt in the solutions (φ_V). The results of the calculations are given in Tables 3, 4, 5, and 6.

In Fig. 5 the relationship between φ_V and $\sqrt{m}$ is shown graphically for the results obtained by us in the present investigation, for the results obtained by us previously [11], and for the results of various other authors. We must mention that an arithmetic error was made in the calculation of the densities of aqueous uranyl nitrate solutions in our preliminary communication [11], which was published some years ago. In Table 7 the corrected values are given.

It will be seen from Fig. 5 that in all previous investigations, with the exception of those of Vasilyev, solutions in a comparatively short concentration range were studied. Examining each author's data separately, we

may make the following comments. The data of Gomez [4] refer to 25°; they cover a short range of concentrations in the high-dilution region (from $\underline{m} = 0.01$ to $\underline{m} = 0.10$) and, as will be seen from Fig. 5, cannot be used for the calculation of φ_V both because of the shortness of the concentration range and also because of the excessively wide scatter of the points. The data of Grant, Darch, Bowden, and Johnes refer to more concentrated solutions than those investigated by Gomez, viz. from $\underline{m} = 0.15$ to $\underline{m} = 0.88$, and they again refer to 25°. It will be seen that the scatter of the points is again too great. Bromer's data are too limited: only two measurements at 19°. Vasilyev's data cover a wide range of concentrations, but, as will be seen, the points do not lie on a straight line, probably because the measurements were not sufficiently accurate in the region of dilute solutions.

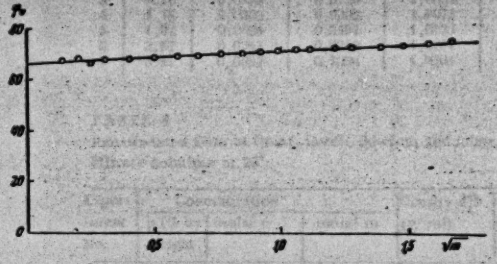

Fig. 4. Relationship between φ_V and $\sqrt{m}$ for aqueous uranyl nitrate solutions at 25°.

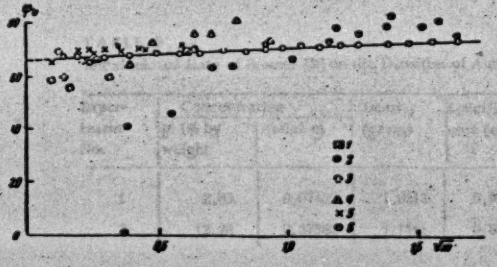

Fig. 5. Relationship between φ_V and $\sqrt{m}$ for aqueous uranyl nitrate solutions according to our data and to recalculated data from the literature: 1) Bromer [2]; 2) Vasilyev [1]; 3) Gomez [4]; 4) Grant, Darch, Bowden, and Johnes [3]; 5) our preliminary results; 6) our final results

As will be seen from Figures 4 and 5, our results cover concentrations ranging from almost saturation to extreme dilution, measurements being taken at very short concentration intervals. The results lie quite satisfactorily on the straight line and can therefore be used as the basis for the determination of the value of φ corresponding to infinite dilution, i.e. $\varphi^0_{VUO_2(NO_3)_2}$. We carried out the extrapolation on the assumption that the points lie on a straight line and the experimental results can be expressed by the equation:

$$\varphi_V = \varphi^0_V + S_V\sqrt{m}, \qquad (2)$$

in which S_V is the proportionality coefficient (the slope of the straight line). The coefficients in Equation 2, φ^0_V and S_V, were found by the method of least squares. As is well known, by this method the sum of the squares of the differences between the calculated and observed values of φ_V is reduced to a minimum.

TABLE 3

Recalculated Data of Gomez [4] on the Densities of Aqueous Uranyl Nitrate Solutions at 25°

Experiment No.	Concentration p (% by weight)	Concentration molar c	Concentration molal m	Density d_4^{25} (g/ml)	Specific volume V_4^{25} (ml/g)	Apparent molar volume φ_V (ml/mole)	$\sqrt{m}$
1	0,41	0,0105	0,0105	1,0006	0,99940	58,0	0,10
2	0,61	0,0155	0,0156	1,0021	0,99799	69,4	0,12
3	0,78	0,0198	0,0199	1,0037	0,99631	59,1	0,14
4	1,18	0,0302	0,0303	1,0073	0,99275	55,4	0,17
5	1,92	0,0494	0,0497	1,0133	0,98687	65,6	0,22
6	2,87	0,0743	0,0749	1,0211	0,97934	70,9	0,27
7	3,81	0,0997	0,1006	1,0304	0,97050	60,0	0,32

TABLE 4

Recalculated Data of Grant, Darch, Bowden, and Johnes [3] on the Densities of Aqueous Uranyl Nitrate Solutions at 25°

Experiment No.	Concentration p (% by weight	Concentration molar c	Concentration molal m	Density d_4^{25} (g/ml)	Specific volume V_4^{25} (ml/g)	Apparent molar volume φ_V (ml/mole)	$\sqrt{m}$
1	5,71	0,1523	0,1543	1,0473	0,95484	65,2	0,39
2	8,40	0,2283	0,2329	1,0703	0,93432	73,5	0,48
3	14,35	0,4107	0,4253	1,1275	0,88692	76,7	0,65
4	16,49	0,4821	0,5010	1,1522	0,86790	72,5	0,71
5	20,56	0,6210	0,6567	1,1903	0,84012	83,2	0,81
6	25,78	0,8260	0,8825	1,2615	0,79271	74,2	0,94

TABLE 5

Recalculated Data of Bromer [2] on the Densities of Aqueous Uranyl Nitrate Solutions at 19°

Experiment No.	Concentration p (% by weight	Concentration molal m	Density (g/ml)	Specific volume (ml/g)	Apparent molar volume φ_V (ml/mole)	$\sqrt{m}$
1	2,85	0,07452	1,0212	0,97924	67,86	0,27
2	12,98	0,37863	1,1161	0,89598	70,60	0,61

The values of φ_V° and S_V were calculated from the formulas:

$$\varphi_V^\circ = \frac{\Sigma m \Sigma \varphi_V - \Sigma(\sqrt{m})\,\Sigma(\varphi_V\sqrt{m})}{n\Sigma m - [\Sigma(\sqrt{m})]^2}, \tag{3}$$

$$S_V = \frac{n\Sigma(\varphi_V\sqrt{m}) - \Sigma(\sqrt{m})\Sigma\varphi_V}{n\Sigma m - [\Sigma(\sqrt{m})]^2}. \tag{4}$$

As a result of the extrapolation the following value was found for the apparent molar volume of uranyl nitrate in aqueous solution:

$$\varphi_{V\,UO_2(NO_3)_2}^\circ = 65,9 \text{ ml/mole}$$

For the slope of the straight line we obtained the value $S_V = 5,23$.

TABLE 6

Recalculated Data of Vasilyev [1] on the Densities of Aqueous Uranyl Nitrate Solutions at 17°

Experiment No.	Concentration p (% by weight	Concentration molal m	Density (g/ml)	Specific volume (ml/g)	Apparent molar volume φ_V (ml/mole)	$\sqrt{m}$
1	2,80	0,07310	1,0257	0,97494	1,2	0,27
2	5,73	0,15424	1,0510	0,95147	41,26	0,39
3	10,92	0,31106	1,1035	0,90621	46,15	0,56
4	14,26	0,42203	1,1288	0,88590	71,79	0,65
5	16,96	0,51826	1,1625	0,86022	63,62	0,72
6	20,05	0,63636	1,1983	0,83452	64,21	0,80
7	25,58	0,87221	1,2599	0,79371	72,90	0,93
8	29,77	1,0756	1,3247	0,75489	66,88	1,03
9	34,88	1,3592	1,3939	0,71741	72,65	1,17
10	37,85	1,5454	1,4295	0,69954	79,35	1,24
11	39,73	1,6727	1,4669	0,68171	76,61	1,29
12	43,11	1,9229	1,5204	0,65772	79,67	1,39
13	44,02	1,9954	1,5275	0,65466	81,45	1,41
14	47,94	2,3367	1,6155	0,61900	79,63	1,53
15	49,92	2,5294	1,6508	0,60584	81,76	1,59
16	52,04	2,7534	1,7118	0,58418	78,13	1,66
17	53,91	2,96805	1,7480	0,57208	80,28	1,72
18	54,77	3,07227	1,7536	0,57026	83,90	1,75

TABLE 7

Densities, Specific Volumes, and Apparent Molar Volumes of Aqueous Uranyl Nitrate Solutions at 25° [11]

Experiment No.	Concentration p (% by weight	Concentration molal m	Density (g/ml)	Specific volume (ml/g)	Apparent molar volume φ_V (ml/mole)	$\sqrt{m}$
1	0,42	0,01058	1,00055	0,99945	63,70	0,10
2	0,42	0,01067	1,00063	0,99937	66,78	0,10
3	1,57	0,04049	1,01014	0,98996	69,55	0,20
4	2,46	0,06408	1,01769	0,98262	70,13	0,25
5	2,71	0,07060	1,01988	0,98051	68,70	0,26
6	3,46	0,09097	1,02626	0,97441	70,38	0,30
7	4,53	0,12043	1,03550	0,96572	71,52	0,35
8	4,97	0,13270	1,03954	0,96196	70,28	0,36
9	7,16	0,19565	1,05940	0,94393	70,38	0,44
10	7,34	0,20103	1,06123	0,94230	69,70	0,45
11	12,38	0,35842	1,10934	0,90144	72,06	0,60
12	12,38	0,35842	1,10948	0,90132	71,68	0,60

The equation relating the apparent molar volume with molality will have the form:

$$\varphi_{V_{UO_2(NO_3)_2}} = 65{,}9 + 5{,}23\sqrt{m}. \qquad (5)$$

For the value of φ_V° found for $UO_2(NO_3)_2$, we may calculate φ_V° for the UO_2^{2+} ion. In the system of Fajans and Johnson [12] $\varphi^\circ_{V_{NO_3^-}} = 29{,}4$, so that:

$$\varphi^\circ_{V_{UO_2^{2+}}} = \varphi^\circ_{V_{UO_2(NO_3)_2}} - 2\varphi^\circ_{V_{NO_3^-}} = 65{,}9 - 58{,}8 = 7{,}1 \text{ ml/g-ion}$$

Hence, the apparent molar volume of the uranyl ion in infinitely dilute solution at 25° is 7.1 ml/g-ion.

SUMMARY

1. A description is given of the determination of densities of aqueous solutions with the aid of a single quartz pycnometer having a capillary neck. The determination is accurate within 0.001%.

2. The densities of aqueous uranyl nitrate solutions were investigated over the concentration range 0.7-52.4% by weight, the results being accurate within 0.01%.

3. The apparent molar volumes of uranyl nitrate in aqueous solutions at 25° were calculated. They can be expressed by the equation:

$$?_{V_{UO_2(NO_3)_2}} = 65{,}9 + 5{,}23\sqrt{m}.$$

4. The apparent molar volume of the uranyl ion UO_2^{2+} was calculated for infinitely dilute aqueous solution at 25°. In the system of Fajans and Johnson it is 7.1 ml/g-ion.

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KINETICS OF THE OXIDATION OF ETHANE IN PRESENCE OF HYDROGEN BROMIDE

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The oxidation of hydrocarbons presents one of the simplest direct means of preparing important products of the heavy organic chemicals industry. However, in spite of the obvious advantages of using oxidation processes for the preparation of aldehydes, ketones, organic acids, alcohols, peroxides, etc., these processes have been realized in industry only in isolated cases.

The existence of this situation is in large measure due to inadequate progress in theoretical investigations into the kinetics and chemistry of oxidation reactions of hydrocarbons; and yet it is through such investigations that we may expect to discover the peculiar features of these oxidation processes, and such knowledge may enable us to make a fresh attack on the problem of the controlled oxidation of hydrocarbons and to solve it. The question of the suitability of a given oxidation process for use in manufacture is mainly resolved purely empirically at present. If change in reaction conditions (temperature, pressure, composition of original mixture, use of catalysts) makes it possible to obtain a satisfactory yield of the desired product, the question is considered to be solved. Such an approach to the solution of the problem is only a first approximation, and a more profound knowledge of the mechanisms of the oxidation processes must reveal new ways of bringing about the reactions, advantage being taken of one or other peculiarity of the mechanism.

In a recent paper [1] one of us discussed the problem of directing chemical reactions and suggested that a contribution to its solution might be made on the basis of the application of some new facts discovered in the homogeneous catalysis of the oxidation reactions of hydrocarbons [2,3]. It was noted that the initiating effect of additions of various substances (homogeneous catalysts) is often associated only with the initial stages of the oxidation processes. The oxidation process, initiated by the addition of a catalyst or initiator (if the added substance is used up) then proceeds as a sequence of two macroscopic stages. Under suitable conditions these stages may be somewhat separated in time, though even then, the second stage will begin while the first is proceeding. It is obvious that, when there is a sequence of macroscopic stages, the oxidation process should be carried out not under conditions that are strictly constant from beginning to end, but under conditions that change during the transition from one stage to the other, so that they are optimum conditions for both stages of the reaction.

The present investigation had the object of discovering the kinetic peculiarities of the oxidation processes of hydrocarbons in presence of hydrogen bromide, the example taken being the oxidation of ethane. The chemical possibilities of the oxidation of hydrocarbons in presence of hydrogen bromide were examined by Rust in a series of papers [4-7]. In our work, we proposed to verify the extent to which the phenomena of limited yields of products and sequences of macroscopic stages are to be found in the mechanism of catalysis with hydrogen bromide, such phenomena having been found in the oxidation of propane, which was investigated by one of us with coworkers [2,3]. Moreover, we wished to establish the kinetic laws of the oxidation reaction of ethane in presence of hydrogen bromide, no information on this being available in the literature.

EXPERIMENTAL

The kinetics of the oxidation of ethane in presence of hydrogen bromide were investigated in a static vacuum apparatus (Fig. 1). An equimolecular mixture of ethane and oxygen was prepared in the flask 1 and a sample was passed into the intermediate vessel 2 until the required pressure was reached, as shown by a mercury manometer. The mixture was transferred by a turn of a tap into the reaction vessel 3, into which, before experiment, hydrogen bromide was introduced from the flask 4. The reaction vessel (diameter 30 mm), which was of ordinary glass, was situated in an electric furnace, the temperature of which was measured with a thermocouple.

The change of pressure in the reaction vessel was observed with the aid of the membrane manometer 5. In order to avoid any distortion of the picture of the pressure variation during the process, due to condensation and partial dimerization of acetic acid at room temperature, the intermediate connections were provided with an electric heater and the manometer space was connected to the reaction vessel only at the moment when the pressure was measured. The apparatus was generally evacuated down to a high vacuum. It should be noted that the reaction studied was found to be only slightly sensitive to the degree of evacuation of the vessel before the experiment.

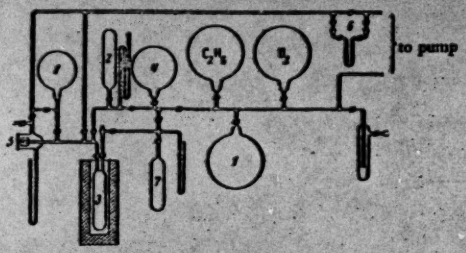

Fig. 1. Diagram of apparatus.

Samples for the analysis of condensable products were obtained by transference of the mixture from the reaction vessel to the trap 6, which was connected through ground joints; this was previously evacuated carefully and cooled. The products condensed in the trap were analyzed for acetic acid, HBr, bromine, aldehydes, and peroxides. Analysis for total acidity was carried out alkalimetrically, phenolphthalein being used as indicator. The hydrogen bromide content was determined by the Volhard method. The amount of acetic acid was determined from the difference between the total acidity and the hydrogen bromide content. Analysis for aldehydes, which was carried out by the hydroxylamine method after previous neutralization of the sample to bromophenol blue with alkali, did not show the presence of aldehydes in the mixture of products. Even the very sensitive qualitative test for aldehydes with Schiff's reagent was negative. The absence of aldehydes was established also polarographically. With the aid of the polarographic method we assured ourselves that organic peroxides were also absent. Analysis for bromine was carried out iodometrically, this being possible in view of the absence of peroxides. This method revealed the presence of a very slight amount of bromine, mainly formed at the beginning of the reaction when it was carried out at low temperatures (215°, 205°).

Kinetic Laws of the Reaction

The kinetics of the oxidation of ethane in presence of hydrogen bromide were studied at temperatures of 205-245° and at pressures of 100-200 mm. At lower temperatures reaction was too slow, and at higher temperatures it was explosive in vessels of ordinary glass. Reaction was accompanied by appreciable reduction in pressure. The change in pressure agreed fairly closely with the stoichiometric equation of the reaction.

$$C_2H_6 + 1.5O_2 = CH_3COOH + H_2O.$$

All the kinetic results given below were obtained by chemical analytical methods adapted to the peculiar requirements of gaseous reactions.

Most of the experiments were carried out at 230°. Fig. 2 shows typical kinetic curves for the formation of acetic acid at this temperature. In these experiments the total pressure of the mixture was kept constant at 200 mm, and the relative amounts of hydrogen bromide and the equimolecular mixture of ethane and oxygen were varied. The kinetic Curve 1 (Fig. 2), which is for a mixture of 80 mm C_2H_6, 80 mm O_2, and 40 mm HBr, was taken as standard, and all the other curves were compared with it. The remaining kinetic curves were obtained with reduced contents of hydrogen bromide and corresponding increased contents of the equimolecular mixture of ethane and oxygen. The compositions of the mixtures for which these kinetic curves were obtained are indicated below Fig. 2. These results confirm conclusions reported in the literature concerning the formation of acetic acid as the main product of the oxidation reaction in presence of hydrogen bromide. Polarograms

of the condensate of reaction products are "empty" with respect to organic peroxides and aldehydes.

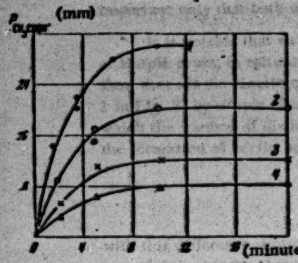

Fig. 2. Kinetic curves for the formation of acetic acid in the oxidation of ethane in presence of various amounts of hydrogen bromide at 230° and p_0 200 mm: 1) 80 mm C_2H_6 + 80 mm O_2 + 40 mm HBr; 2) 85 mm C_2H_6 + 85 mm O_2 + 30 mm HBr; 3) 90 mm C_2H_6 + 90 mm O_2 + 20 mm HBr; 4) 95 mm C_2H_6 + 95 mm O_2 + 10 mm HBr.

Information on the consumption of hydrogen bromide during reaction under the conditions corresponding to Fig. 2 is of interest; this information is given in Fig. 3. As noted previously [8] for the oxidation of propane, hydrogen bromide is consumed only for a short time at the beginning of the reaction; its concentration then becomes constant during the further course of the process (Fig. 2, Curve 3). Owing to the small scale on which the consumption of hydrogen bromide occurs, it is impossible to arrive at any conclusion concerning the kinetic law of its reaction and of the formation of organobromine compounds.

It is evident that the lower the content of hydrogen bromide in the mixture, the less of it is used in the formation of organobromo compounds. In the case of the formation of acetone by the oxidation of propane in presence of hydrogen bromide it was shown that the formation of bromo compounds was a side reaction when considered in relation to the formation of acetone. The formation of the main reaction product, acetone, bore practically no relation to the consumption of hydrogen bromide. In view of the fact that an identical kinetic picture was found in the oxidation of ethane, there is every reason to suppose that the formation of acetic acid also does not demand the consumption of hydrogen bromide, the consumption of which is associated with a side reaction in which bromo compounds are formed.

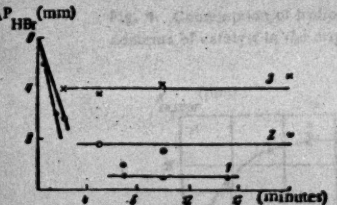

Fig. 3. Consumption of hydrogen bromide in the oxidation of ethane in mixtures differing in initial HBr content. The mixtures are 80 mm C_2H_6 + 80 mm O_2 + the following amounts of HBr: 1) 40 mm; 2) 30 mm; 3) 10 mm.

It is important to note that with further increase in the hydrogen bromide content, the consumption of hydrogen bromide does not increase (Fig. 4). These experiments were carried out at 230°; a constant amount of an equimolecular mixture of ethane and oxygen (80 mm C_2H_6 + 80 mm O_2) was taken, and to this hydrogen bromide was added in greater and greater amounts (from 10 to 90 mm). In the same experiments the yields of acetic acid were determined at the end of the reaction, and the results again confirmed the existence of a limit to the extent to which the original fuel will enter into oxidation reactions [9] (about 50% of the fuel is consumed). Our experiments provided a further, very clear demonstration of this widely found phenomenon, the mechanism of which has not yet been elucidated. Fig. 5 shows the relation between the yields of acetic acid and the hydrogen bromide content of the mixture. It will be seen that, with additions of hydrogen bromide corresponding to pressure increases of more than 30-35 mm, the yield of acetic acid ceases to rise, its value then being 32 mm, i.e. 40% on the original ethane. When we take account of the fact that the formation of acetic acid is accompanied by the formation of a certain amount of other oxidation products, it is again evident that not more than 50% of the original hydrocarbon reacts in the oxidation process.

It is important to note that kinetic curves of the type shown in Fig. 2 are obtained not only when the catalyst content of the mixture is varied, but also when the relative amounts of the other components (ethane and oxygen) are varied. Fig. 6 shows the kinetic curves determined for constant catalyst content (40 mm HBr) and total pressure of the mixture (p_0 = 200 mm), but varying relative amounts of ethane and oxygen. Both the course of the kinetic curves and the yields of acetic acid were completely identical for both cases, but the extent of reaction was less than for the standard mixture (80 mm C_2H_6 + 80 mm O_2 + 40 mm HBr). It was found that ethane and oxygen – at least, for variation of concentration over the range indicated – behave identically. It is

important only that both of these components should be present.

It is notable that the kinetic curves in Figures 2 and 6 are reminiscent of the kinetic curves of reactions of simple types, in spite of the fact that we are dealing with a complex three-component system. It is easy to show that all the kinetic curves in Figures 2 and 6 can be brought into coincidence with one of them, say Curve 1 in Fig. 2, by simple change in the scale of ordinates. The result of such a superposition is shown in Fig. 7, in which the method of distinguishing the points is the same as in Figures 2 and 6. It is not difficult to show that the formation of acetic acid at 230° is described satisfactorily by the kinetic law of a first-order reaction:

$$p_{CH_3COOH} = (p_{CH_3COOH})_\infty (1 - e^{-kt}) \qquad (1)$$

with this difference, however, that as a measure of complete conversion we take not the initial concentration of one of the reactants, but the amount of the final reaction product formed toward the end of the process $(pCH_3COOH)_\infty$.

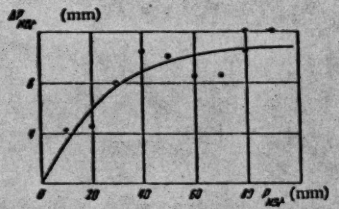

Fig. 4. Consumption of hydrogen bromide at different contents of catalyst in the original mixture.

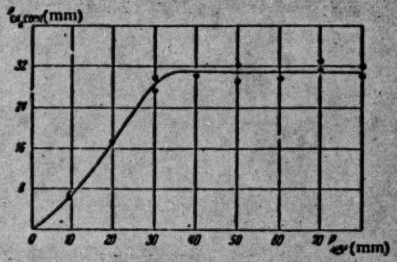

Fig. 5. Relation between the yield of acetic acid in the oxidation of ethane and the HBr content of the mixture. The limit phenomenon for the conversion of ethane into acetic acid.

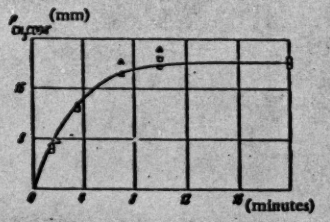

Fig. 6. Kinetics of the formation of acetic acid in the oxidation of ethane in presence of hydrogen bromide for different relative amounts of ethane and oxygen in the original mixture: Δ) 120 mm C_2H_6 + 40 mm O_2 + 40 mm HBr; □) 40 mm C_2H_6 + 120 mm O_2 + 40 mm HBr.

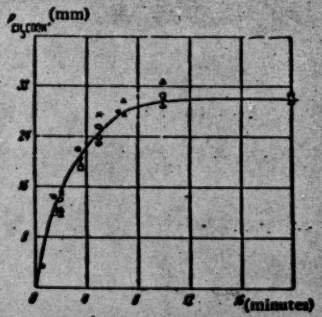

Fig. 7. Superposition of kinetic curves for the formation of acetic acid at 230° from different proportions ethane, oxygen, and hydrogen bromide with the kinetic Curve 1 in Fig. (2).

If we write $$\frac{p_{CH_3COOH}}{(p_{CH_3COOH})_\infty} = \alpha, \qquad (2)$$

then the first-order equation can be written

$$\alpha = 1 - e^{-kt}. \qquad (3)$$

In this form the fundamental property of unimolecular reactions can be clearly seen: the time required for a definite degree of conversion α to be attained does not depend on the initial concentration of the reactant (in our case, on the final yield of acetic acid) and is determined only by the value of k. In fact,

$$t_\alpha = \frac{1}{k}(1-\alpha), \qquad (4)$$

i.e. in the expression for t_α there are no quantities other than α and k (which is determined by the temperature).

In Fig. 8. the kinetic curve of Fig. 7 is presented in the coordinates log $(1-\alpha)$ and t. The linearity of this relationship is a good illustration of the applicability of the first-order law to the description of the kinetics of the reaction. This result is seen to be very important when examined in the light of the analogy with the kinetic law for the formation of acetone in the oxidation of propane in presence of hydrogen bromide. It is indeed surprising that it is not the initial concentration of a reactant that enters the first-order equation, but the concentration of a product at the end of the reaction. By making use of the analogy with the oxidation reaction of propane, we may form an idea of what kind of mechanism can lead to the kinetic laws observed in the experiments. Let us suppose that, in the initial period of the reaction, a macroscopic reaction occurs which is fairly fast, does not occur on a very large scale, and is markedly self-retarding. We will assume that this initial reaction results in the formation of some intermediate Product I of as yet unknown chemical identity in a concentration of I_0. We will assume also that the intermediate Product I, in decomposing in accordance with a unimolecular law

$$I = I_0 e^{-kt}, \qquad (5)$$

forms an ethyl radical C_2H_5 in each act of decomposition:

$$I \rightarrow C_2H_5.$$

The C_2H_5 radical initiates an oxidation chain:

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2;$$

$$C_2H_5O_2 + C_2H_6 \rightarrow C_2H_5O_2H + C_2H_5;$$

$$C_2H_5O_2H \rightarrow CH_3CHO + H_2O$$

$$(\text{or } C_2H_5O_2 \rightarrow CH_3CHO + OH$$

$$OH + C_2H_6 \rightarrow C_2H_5 + H_2O),$$

$$2CH_3CHO + O_2 (\text{in presence of HBr}) \rightarrow 2CH_3COOH.$$

Hence, at each act of decomposition of the intermediate Product I, a chain of reactions is formed and results in the formation of acetaldehyde, which is very rapidly oxidized to acetic acid in presence of hydrogen bromide [10].

If the chain length is ν, then in the decomposition of $I_0 - I$ molecules of the intermediate product

$$(I_0 - I)\nu = I_0\nu(1 - e^{-kt}) \qquad (6)$$

molecules of acetic acid are formed. When we compare Equations 1 and 6, we see that they are completely identical, $(pCH_3COOH)_\infty$ being equal to $I_0\nu$. In other words, the yield of acetic acid at the end of the reaction $(pCH_3COOH)_\infty$ is directly related to the initial concentration of the intermediate product I_0. Hence, the peculiar form of the first-order law (1) receives a simple explanation.

Less definite conclusions can be drawn from a study of the kinetics of the reaction at different temperatures. Above 230° the first-order law for the formation of acetic acid still holds as before (Fig. 9). Below 230°, however, there are departures from this law (Fig. 10), and the curve determined at 205° is a typical kinetic curve for a zero-order reaction.

Hence, our results indicate a change in the kinetic law with fall of temperature (transition from a first-order to a zero-order law). As the kinetic law of the reaction is different at different temperatures, it did not appear to be possible to calculate the activation energy of the process from the temperature-dependence of the rate constant k. An evaluation of the activation energy from the two constants $k_{230°} = 0.84 \cdot 10^{-2}$ second $^{-1}$ and $k_{245°} = 1.2 \cdot 10^{-2}$ second $^{-1}$ gives the value E = 23 kcal/mole. This value for the activation energy is fairly close to that obtained for the oxidation of propane in presence of hydrogen bromide (25 kcal/mole).

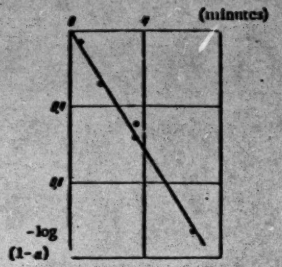

Fig. 8. Semilogarithmic anamorphosis of the kinetic curve of Fig. 7.

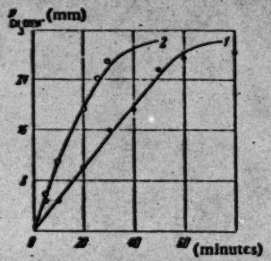

Fig. 10. Kinetic curves for the formation of acetic acid at: 1) 205°; 2) 215°.

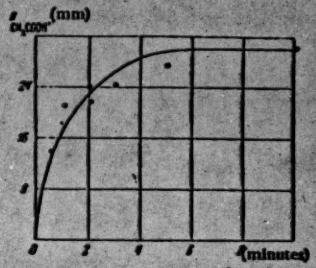

Fig. 9. Kinetic curve for the formation of acetic acid at 245°.

A study was made also of the effect on the reaction of additions of the final product (acetic acid), and also of acetone and acetaldehyde. The additives were held in the flasks indicated as 7 and 8 in the diagram of the apparatus. Acetone was added with the object of determining whether this substance is a specific "poison" for all oxidation reactions carried out in presence of hydrogen bromide. It was hoped that the experiments with acetaldehyde would provide further confirmation of our conclusion that acetaldehyde is very rapidly oxidized to acetic acid in presence of hydrogen bromide.

It is shown that additions of acetic acid, though in very small amount (11.2 mm, which corresponds to the saturated vapor pressure of acetic acid at room temperature), have no effect on the final yield of acetic acid. In other words, the amount added simply forms an addition to the amount of acetic acid formed as a result of the reaction. It must be pointed out, however, that the addition of acetic acid was small, and the experiments on the addition of acetic acid must be regarded as preliminary work.

The experiments on the addition of acetone were almost negative. Acetone, therefore, is not a specific "poison", general for all oxidation reactions of hydrocarbons in presence of hydrogen bromide. The experiments with additions of acetaldehyde (about 5 mm) showed that the whole of the added acetaldehyde was rapidly oxidized to acetic acid, without having any supplementary initiating effect on the oxidation process. Hence, a stage in which acetaldehyde formed as an intermediary in the oxidation of ethane, is rapidly converted into acetic acid is quite possible when hydrogen bromide is present in the system.

Sequence of Macroscopic Stages in the Mechanism of the Reaction

In previous investigations [3,11], the method used for determining the sequence of macroscopic stages in oxidation reactions of hydrocarbons initiated by homogeneous catalysts was based on a study of the heat evolved in the reaction mixture during the reaction, and the scheme of procedure proposed by Kovalsky and Bogoyavlenskaya [12] was adopted. In our work we adopted the same scheme of procedure. If a homogeneous reaction associated with evolution of heat is proceeding in a gas, then under stationary conditions the temperature distribution over the radius of a cylindrical reaction vessel will be determined by a known differential equation:

$$\frac{d^2T}{dr^2} + \frac{1}{r}\cdot\frac{dT}{dr} + \frac{q_v}{\lambda} = 0, \qquad (V)$$

in which T is the temperature of the reaction mixture at a distance r from the center, λ is the thermal conductivity, q_1 is the heat evolved by chemical reaction in 1 cc of the mixture per second. Assuming, as is usual, that q_1 is independent of temperature, and setting the limiting conditions: 1) $T = T_0$ when $r = R$ (T_0 is the temperature of the walls of the vessel, and R is the radius of the vessel); 2) $\left(\frac{dT}{dr}\right)_{r=0} = 0$ (maximum temperature in the center of the vessel), we obtain the following integral for the differential equation (7):

$$T - T_0 = \frac{q_1}{4\lambda}(R^2 - r^2). \tag{8}$$

The rise in temperature in the center, on the axis of the vessel, will be

$$\Delta T_m = \frac{q_1}{4\lambda} R^2. \tag{9}$$

The rate of evolution of heat q_1 is equal to the product of the reaction rate w and the heat of reaction Q of the corresponding process, provided that these quantities are expressed in corresponding units. If the rate of the chemical reaction w is expressed in millimeters of mercury per second for an experiment carried out at a temperature of T_1, then we obtain the following expression for ΔT_m:

$$\Delta T_m = \frac{QwR^2}{4 \cdot 760 \cdot 22\,400 \cdot \lambda} \cdot \frac{273}{T_1}. \tag{10}$$

In calculations from this formula, Q must be expressed in cal/mole and λ in cal/cm. sec. degree. It will be seen from Equation 10 that, in determining the rise in temperature ΔT_m in the center of the vessel as a function of time, we are in fact measuring the reaction rate w, which is proportional to this rise. It will be clear that, if there is a sequence of macroscopic stages separated in time in the process studied, then, in studying the warming up of the reaction mixture during the reaction, we may hope to register two processes of heat evolution reflecting the existence of these stages. This hope was in fact realized in the study of the oxidation of propane to acetone in presence of hydrogen bromide.

The oxidation of ethane to acetic acid is accompanied by evolution of heat (Q = 144 kcal/mole). On analogy with the oxidation reaction of propane, it may be supposed that the initiating reaction, which is probably a branched-chain oxidation process, will also be associated with evolution of heat. We made a continuous photorecord of the galvanometer readings of the thermocouple current corresponding to the different values of ΔT_m during the reaction (composition of mixture: 100 mm C_2H_6 + 100 mm O_2 + 50 mm HBr). The very first photorecord that we made of the reaction at 266° showed two clearly defined maxima on the heat-evolution curve (Fig. 11). Timing marks (the vertical lines) are made every 30 seconds. It will be seen from the photorecord that, in the case under examination, in spite of the fairly high temperature, the initiating reaction – though rapid in comparison with the process as a whole – is still somewhat slow. For this reason the kinetic curve for the formation of acetic acid (in the vessel in which this study of heat evolution in the initial stage of the process was made) departs somewhat from the form required for a first-order law and approximates to a kinetic curve of the type shown in Fig. 10, i.e. to a curve for a zero-order reaction. It must be pointed out that the vessel in which the heat evolution was studied was made of quartz glass, whereas previous experiments were carried out in a vessel of ordinary glass. It is notable, however, that the fall of the heat-evolution curve after the second maximum (Fig. 11), i.e. definitely after the completion of the initiating reaction, corresponds with extreme exactness to the law

$$\Delta T_m \sim e^{-kt}, \tag{11}$$

which corresponds to a unimolecular law for the decomposition of the intermediate reaction product. The value of k, which is determined from the slope of the semilogarithmic anamorphosis of the fall on the heat-evolution curve, is found to be $2.6 \cdot 10^{-2}$ second $^{-1}$. Also, from the values of the constant found for 230° and 245°, it may be inferred that a value of $2.9 \cdot 10^{-2}$ second $^{-1}$ is to be expected at 266°. This agreement between the constants for the rate of decomposition of the intermediate compound in completely different vessels indicates the homogeneous character of this reaction and of the associated process of formation of acetic acid.

The conclusion that the second stage is homogeneous is confirmed also by a comparison between the heat evolution calculated on the assumption of a completely homogeneous reaction and the heat evolution observed

experimentally. Substituting in Equation 10 the mean value of the thermal conductivity of the reacting gases (ethane, oxygen, hydrogen bromide) $\lambda \approx 8 \cdot 10^{-5}$ cal/cm. sec. degree, $Q = 144000$ cal/mole, $T_i = 539°K$, $R = 1.5$ cm, and the rate of formation of acetic acid corresponding to the time of attainment of the second maximum of heat evolution, which was found to be $\underline{w} = 0.22$ mm/second, we find that

$$\Delta T_m = \frac{144\,000 \cdot 0{,}22 \cdot 2{,}25 \cdot 273}{4 \cdot 760 \cdot 22\,400 \cdot 8 \cdot 10^{-5} \cdot 539} = 6{,}8°.$$

Experiment gives $\Delta T_m = 7.0°$, the agreement being extremely close.

As regards the nature of the initiating reaction, it is undoubtedly a homogeneous-heterogeneous process. The high sensitivity of the extent and duration of the initiating reaction to the state of the vessel surface indicates that its mechanism includes elementary processes associated fundamentally with the wall. At the same time the considerable rise of temperature at the central thermocouple indicates a predominant homogeneous component in the initiation process. Thus, a study of heat evolution in the reaction mixture during the reaction permitted us to establish that, in this case also, there is a sequence of macroscopic stages, displaced from one another in time, in the mechanism of the catalytic process.

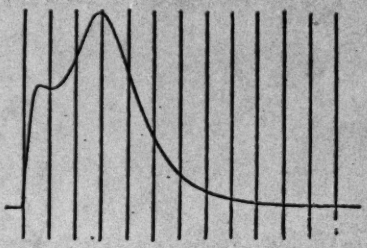

Fig. 11. Photorecord of heat evolution in the reacting mixture of 266°.

SUMMARY

1. A study was made of the kinetic laws of the oxidation of ethane to acetic acid in presence of hydrogen bromide. It was shown that the process of acetic acid formation comes to an end long before the reactants are used up. Such "limit phenomena" are explained on the basis of the existence of an initiating reaction that results in the formation of an intermediate product, the amount of which determines the yield of acetic acid.

2. It was established that, whatever method is adopted for initiating the oxidation process by additions of catalyst (hydrogen bromide), the yield of acetic acid cannot be raised above 40% on the amount of ethane taken. The generality of the phenomenon was pointed out; it is found in other slow-oxidation reactions.

3. With the aid of a method based on the study of the evolution of heat in the reaction mixture during the reaction it was shown that the mechanism of the reaction includes a sequence of two macroscopic stages displaced from one another in time. The first stage – the initiating reaction – is a homogeneous-heterogeneous process. The second stage – the formation of acetic acid initiated by the decomposition of the intermediate product obtained in the first stage – is a homogeneous process. These results confirm the prevalence of the phenomenon of successive macroscopic stages in oxidation processes initiated by additions of homogeneous catalysts.

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RELATION BETWEEN THE CATALYTIC ACTIVITY OF BINARY COMPOUNDS OF GROUP II METALS WITH NONMETALS AND THE POSITIONS OF THE ELEMENTS IN MENDELEEV'S PERIODIC SYSTEM

COMMUNICATION 1. CATALYTIC DECOMPOSITION OF ISOPROPYL ALCOHOL OVER ALKALINE-EARTH OXIDES

O. V. Krylov, S. Z. Roginsky, and E. A. Fokina

The comparative study of the two directions of decomposition of isopropyl alcohol over various catalysts

$$C_3H_7OH \rightarrow CH_3COCH_3 + H_2 \quad (1)$$

$$C_3H_7OH \rightarrow CH_3CH=CH_2 + H_2O \quad (2)$$

is of great interest for the elucidation of the laws governing the selection of catalysts. In this case, to the usual criterion of catalytic activity we must add selectivity criteria.

According to the classification of catalytic reactions developed in our laboratory [1,2], the first of these reactions (dehydrogenation) can be treated as a reaction of the oxidation-reduction (electronic) type. The data of Myasnikov and Pshezhetsky on the proportionality between the electrical conductivity of zinc oxide and its catalytic activity in this reaction [3] confirm this view. It is natural to regard the second direction of decomposition (dehydration) to be a reaction of the acid-base (ionic) type. This view is confirmed by the considerable increase in decomposition in this direction under the action of small amounts of acids and acid salts held by the catalyst [4,5].

It appears, therefore, that the two directions of decomposition, corresponding to Equations 1 and 2, are representative of two main types of catalysis mechanisms. If this inference is true, the ratio of the rates of the two reactions can be used to characterize the relative efficiencies of a given catalyst in the promotion of the two types of reactions – oxidation-reduction and acid-base.

For our problem, solids of marked chemical properties are of primary interest. The papers that have appeared on the alcohol-decomposition reaction [6-8] contain many data on the catalytic properties of typical acid oxides and oxides of the transitional elements, but there is an almost complete absence of information on the catalytic properties of oxides of the alkaline type (oxides of alkali and alkaline-earth metals) in this process. As a part of the scheme for the systematic study of the dependence of the catalytic properties of solids on the positions of the elements forming them in Mendeleev's periodic system, it was desirable to fill this gap in our knowledge. The present investigation was devoted to a study of the decomposition of isopropyl alcohol over alkaline-earth oxides – CaO, SrO, and BaO.

As alkaline-earth oxides readily absorb water vapor and carbon dioxide, it was necessary to take account of the possibility that the catalytic reaction would occur not only on the surface of the oxide, but also on a carbonate or hydroxide film. Supplementary experiments were therefore carried out on the decomposition of isopropyl alcohol on the corresponding hydroxides and carbonates.

EXPERIMENTAL

Preparation of catalysts. Two samples of calcium oxide were used. The first sample was prepared from the hydroxide by calcination in a vacuum at 800°, the hydroxide being first prepared by the action of steam at 100° on calcined calcium oxide. The second sample was laboratory-reagent calcium oxide (chemically pure grade). Strontium oxide was prepared by precipitation of the hydroxide from strontium nitrate solution with caustic soda, washing of the precipitate, and calcination in a vacuum at 800°. Barium oxide was prepared by decomposition of the peroxide in a vacuum at 800°. The following catalysts were also tested: calcium hydroxide, prepared by precipitation from calcium nitrate solution with caustic soda and washing with water with exclusion of carbon dioxide; barium carbonate (chemically pure grade); and calcium carbonate (chemically pure grade).

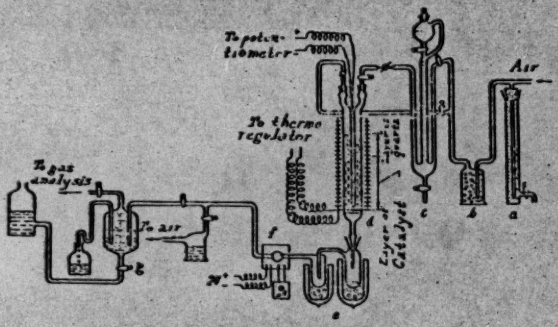

Fig. 1. Diagram of flow apparatus for the study of the catalytic decomposition of isopropyl alcohol: (a) manostat; (b) vessel containing silica gel for purifying the air; (c) apparatus for introduction of alcohol; (d) quartz reactor; (e) traps for freezing out liquid reaction products; (f) gas analyzer; (g) calibrated gas holder for collecting gaseous reaction products.

The surface areas of the catalysts were determined on a quartz spring balance by measuring the adsorption of n-heptane vapor at 20°. The area occupied by a heptane molecule was taken to be 59 A^2 [9]. Calculations based on the resulting adsorption isotherm were made by the "BET" method. Depending on the sensitivity of the quartz spring used, the determined specific surfaces were accurate within 2-8 m^2/g.

Before being introduced into the reactor, the catalyst was kneaded with anhydrous isopropyl alcohol and made into tablets, 3-4 mm in diameter and 5-7 mm in length. In some experiments larger tablets were used (up to 10 mm in diameter). Increase in the size of the tablets had practically no effect on the character of the catalytic decomposition of isopropyl alcohol; this fact appears to exclude the possibility that the rate of the process may be controlled by diffusion.

Decomposition of isopropyl alcohol. The reaction was studied in a flow apparatus, which is shown diagrammatically in Fig. 1. The introduction of the alcohol was effected automatically with the aid of compressed air at constant pressure. The rate at which the alcohol was introduced varied from 0.07 to 1.08 ml/minute in various experiments, and in the majority of the experiments it was in the narrower range of 0.27-0.32 ml/minute. The catalyst (25 ml) was placed in a quartz reactor and was covered with a layer (15-20 mm) of broken quartz in order to ensure complete evaporation of the isopropyl alcohol and the better distribution of its vapor through the catalyst. Before the experiment the isopropyl alcohol (chemically pure grade) was allowed to stand over anhydrous copper sulfate and was then distilled (b.p. 81-82°). The temperature was maintained constant within 0.5° with the aid of an ERM-47 thermoregulator. The condensable reaction products and unchanged alcohol were frozen out in two traps cooled with snow. The gaseous reaction products were analyzed continuously with the aid of a gas analyzer based on the measurement of the thermal conductivity of the mixture

and calibrated with various hydrogen-propene mixtures. Also, determinations were made periodically in order to find the content of unsaturated hydrocarbons in the gas; the analysis was carried out in a "VTI" apparatus with bromine water or a solution of mercuric sulfate in concentrated sulfuric acid.

Experimental Results

The table gives the results of experiments on the catalytic decomposition of isopropyl alcohol over the catalysts studied. Column 4 of the table gives the overall rate of gas formation (propene + hydrogen). Column 5 gives the percentage content of unsaturated compounds (propene) in the gas. The figures given here refer to the stationary state, which was generally established after 0.5-2 hours. During this period there was a small fall in the reaction rate and an increase in the yield of unsaturated hydrocarbons. It should be noted that this change in the reaction rate at the beginning of the process was considerably less than that generally observed in the decomposition of alcohols on acid oxides and oxides of transition metals. No carbonization of the catalyst was observed, and there was no visible change in its color. Nevertheless, before each experiment– to remove adsorbed compounds and to bring the catalyst into a standard condition– air was blown over the catalyst at 500°. Columns 6 and 7 give values of the activation energies for dehydrogenation E_{H_2} and for dehydration E_{H_2O} in cal/mole; they were calculated from graphs for the relation between the logarithm of the rate of formation of hydrogen or propene, respectively, and the reciprocal of the temperature (the rate of passage of alcohol being constant). A study of the relation between the rate of gas formation and the time of contact (determined from the rate of passage of alcohol) showed that, at low and medium rates of passage of alcohol, the decomposition follows a first-order law. This fact enables us to calculate activation energies directly from the data presented in the table. The last column gives values of the "selectivity coefficient", which is the ratio of the yield of hydrogen to that of propene at the given temperature (calculated directly from the data in Column 5).

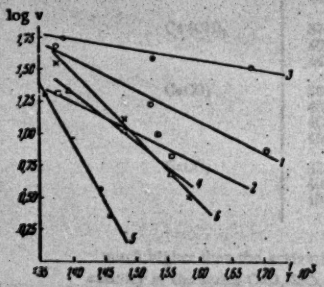

Fig. 2. Determination of the activation energies for the dehydrogenation of isopropyl alcohol over the catalysts: 1) imported CaO; 2) SrO; 3) BaO; 4) $Ca(OH)_2$; 5) $CaCO_3$; 6) $BaCO_3$.

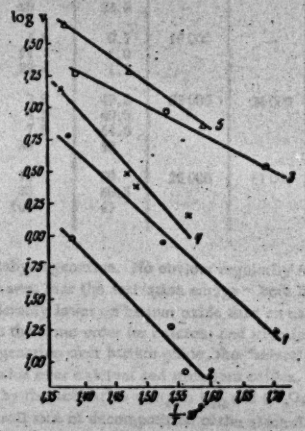

Fig. 3. Determination of the activation energies for the dehydration of isopropyl alcohol over the catalysts: 1) imported CaO; 2) SrO; 3) BaO; 4) $CaCO_3$; 5) $BaCO_3$.

Fig. 2 gives the straight-line graphs for the relation between the logarithm of the rate of gas formation and the reciprocal of the temperature, and, with the aid of these, values of the activation energy for dehydrogenation were calculated. Fig. 3 gives the corresponding straight lines for the calculation of the activation energies for dehydration. The points in Fig. 3 have a wider scatter than those in Fig. 2, this being due to the inadequate accuracy of the experiment.

These experimental data show that the oxides of the main sub-group of Group II of the periodic system have appreciable catalytic effect on the decomposition of isopropyl alcohol. These oxides (CaO, SrO, and BaO), like the oxides of elements of the secondary sub-group [6,7,8], have a predominantly dehydrogenating effect. The activation energy for dehydrogenation is not great; ranging from 6000 cal/mole for BaO to 16,000 cal/mole for CaO obtained by decomposition of the hydroxide. The activation energy for dehydration is high

TABLE

Experimental Results on the Decomposition of Isopropyl Alcohol over Alkaline-earth Oxides and Their Derivatives

Catalyst	Temperature (°C)	Specific surface (sq.m/g)	Rate of gas formation (ml gas per ml alcohol per minute)	Propene content of gas (%)	Activation energy for dehydrogenation E_{H_2} (cal/mole)	Activation energy for dehydration E_{H_2O} (cal/mole)	Selectivity coefficient K_{H_2}/K_{H_2O}
1	2	3	4	5	6	7	8
Imported CaO	314	18	8	2.3	12 000	22 000	43
	384		17	4.9			19
	453		57	13.6			6.4
CaO made from hydroxide	358	72	21.4	2.8	16 000	26 000	35
	386		30.8	3.6			27
	400		53.5	6.4			15
	436		71	7			13
SrO	370		6	1.3	11 000	25 000	76
	377	5	11	1.7			58
	452		21	4.7			20
BaO	320	17,5	38	9.2	6 000	12 000	9.9
	382		48	19.3			4.2
	448		69	24.3			3.1
$Ca(OH)_2$	370	24	4.8	0.7	16 000	—	142
	400		11	1.0			99
	442		22	1.1			90
$CaCO_3$	366	< 5	3.0	49.5	39 000	24 000	1.02
	404		4.5	49.5			1.02
	428		7.0	44.5			1.25
	460		35	42			1.38
$BaCO_3$	358		10	70	26 000	17 000	0.43
	404	< 5	33	60.5			0.65
	454		100	47			1.13

— much higher than the activation energy for dehydrogenation. No obvious regularity is to be observed in selectivity in the series CaO, SrO, BaO. It can be seen that the activation energy — both for dehydrogenation and for dehydration of isopropyl alcohol — is considerably lower on barium oxide than on calcium and strontium oxides. On the other hand, these quantities are the same order for calcium and strontium oxides. In spite of the low value of activation energy for dehydrogenation over barium oxide, the "selectivity coefficient" over barium oxide has only about one-tenth of its value over calcium and strontium oxides. This indicates that the variation in selectivity is determined not only by the activation energies E_{H_2} and E_{H_2O}, but also by the pre-exponential factors K_{H_2} and K_{H_2O}. The overall rate of decomposition of the alcohol (rate of gas formation); expressed per unit surface area at the given temperature, rises in the series CaO, SrO, BaO, i.e. with rise in the atomic weight of the metal.

On freshly prepared calcium hydroxide the rate and selectivity of the process are close to the corresponding characteristics for the decomposition of the alcohol on the pure oxide. The activation energy for dehydrogenation over the hydroxide is very close to E_{H_2} over calcium oxide. Dehydration proceeds very feebly. Over the temperature range studied, the rate of dehydration over carbonates is close to the rate of dehydrogenation. This catalyst differs greatly from the others in that the activation energy for dehydrogenation is high and is considerably higher than the activation energy for dehydration, and the selectivity coefficient is close to or less than unity.

Discussion of Experimental Results

The closeness of the activation energies for dehydration over carbonates (24,000 cal/mole for $CaCO_3$

and 17,000 cal/mole for $BaCO_3$) to the corresponding values for oxides (22,000-26,000 cal/mole for CaO and 12,000 cal/mole for BaO) makes it probable that the slight dehydration over alkaline-earth oxides (considerable in the case of BaO) is due to partial coverage of the oxides with a carbonate film; in themselves, the oxides have very marked dehydrogenating action. This is probably a special case of the effect of captured anions on the catalytic properties of solids. It is probable that this effect is met in catalysis just as frequently as the effect of cations, but the deforming action of the latter is stronger owing to their smaller radii and is therefore more frequently observed. The position of hydroxides is different; they are always present during the catalytic decomposition of alcohols because water is one of the decomposition products and the equilibrium temperature for the decomposition of the hydroxide is higher than the reaction temperature. The closeness of the values of the activation energies for dehydration over CaO (12,000-16,000 cal/mole) and over $Ca(OH)_2$ (16,000 cal/mole) confirms this view.

The powerful catalytic dehydrogenating action that we have found in solid alkalis used as catalysts for the decomposition of alcohols does not appear to have been specially emphasized by anyone previously. We know only of an observation by Eucken [7], who noted the 100% predominance of dehydrogenation in the decomposition of ethanol over calcium oxide. In this connection we may mention that Zhabrova and Kutseva, in collaboration with one of the present authors [4], showed that the dehydrogenating action of zinc oxide was increased by alkaline additions. The presence of alkaline additions may be the explanation also of the increase in dehydrogenating power observed when alumina prepared by alkaline precipitation was ignited in the experiments of Boreskov and coworkers [10]. Owing to the reduction in the surface area during ignition, the surface concentration of alkali might have been increased in this sample. According to the results of Ohta and Sato [11], the alkaline treatment of metal catalysts suppresses the dehydration of cyclohexanol, but does not affect the rate at which it is dehydrogenated.

Until now, attention has generally been turned on the poisoning effect of alkalis on acidic catalysts (mainly aluminosilicate catalysts for the cracking of hydrocarbons). However, isolated examples can be found in the literature in which alkaline additions have powerful promoting effects on other reactions, which, according to the accepted classification, belong to the oxidation-reduction (electronic) type. For example, alkaline additions increase the activity of oxide catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen [12] and for the synthesis of alcohols [13], and they increase also the activity of metal catalysts in hydrogenation reactions [14]. Alkalis accelerate the decomposition of hydrogen peroxide [15] and of ozone [16]. The results of some Japanese investigators indicate that alkalis have an accelerating effect also on some reactions of solids having a similar mechanism to oxidation-reduction reactions. Thus, exchange between oxygen and water proceeds considerably more rapidly on alkaline-earth oxides then on any other oxides, including electronic semiconductors [17]. Alkaline additions accelerate the surface oxidation of carbon [18] and the reduction of ferric oxide with carbon [19].

Comparison of the data in the literature with our results on the dehydrogenation of isopropyl alcohol over solid alkalis leads to the view that catalysis over alkalis is a very prevalent phenomenon. It is a phenomenon that has received very little study, owing to the fact that special methods are required for bringing it about; this arises from the difficulty of preparing alkaline catalysts of high specific surface and the difficulty of keeping them unchanged over a long period. It is probably for this reason that such catalysis has not found wide use in industry. The existence of a special kind of catalysis over alkalis is supported by the rise in catalytic activity with increase in the alkalinity of the oxide in Group II of the periodic system (with increase in the atomic weight of the metal forming the oxide).

Various mechanisms may lie behind the catalytic activity of alkalis:

1. The usual acid-base interaction is possible; with proton transfer as for acid catalysts, but in the opposite direction.

2. Alkaline-earth oxides may act as electronic oxides – semiconductors – with electron transfer at the determining stage. It should be noted that, according to the investigations of Hauffe and Tranckler [20], calcium oxide has semiconductor properties and, under various conditions, can be both an electronic and a "hole" semiconductor. It is not clear, however, whether such a mechanism is possible for the hydroxides $M(OH)_2$, which, according to our results, act in the same way as the oxides MO.

3. It is possible, however, that there is no real antithesis between the first two mechanisms, there being some sort of correlation between the electron-hole and acid-base properties of a solid body. According to the

theory of electrophilic and nucleophilic reactions, there is no fundamental difference between oxidation-reduction and acid-base reactions; but acid and base, on the one hand, and oxidizing agent and reducing agent, on the other, are only special cases of the more general concept of donor and acceptor.

In order to make a choice between these possibilities it is necessary in the first place to carry out experiments with other, still stronger alkalis derived from metals of Group I of the periodic system; such experiments will at the same time indicate the prevalence of catalysis among solid alkalis. It is desirable also to measure the electrical properties of the solid alkaline hydroxides MOH and $M(OH)_2$, though this task will meet great experimental difficulties.

SUMMARY

1. The catalytic activity and selectivity of calcium, strontium, and barium oxides, calcium and barium carbonates, and calcium hydroxide in the decomposition of isopropyl alcohol were studied at atmospheric pressure over the temperature range 314-460° in a flow apparatus.

2. In the series CaO, SrO, BaO the catalytic activity of the oxide rises with increase in the atomic weight of the metal. Over all these oxides, dehydrogenation predominates over dehydration. The activation energies for dehydrogenation over the oxides are less than the activation energies for dehydration.

3. The activation energy for the dehydration of isopropyl alcohol is the same over the oxides of the alkaline-earth metals as it is over the corresponding carbonates. On the basis of this fact it is suggested that carbonate impurities present in the oxides are responsible for dehydration.

4. In the decomposition of isopropyl alcohol over calcium oxide and calcium hydroxide, the activation energies for dehydrogenation are very close in value (12,000-16,000 cal/mole).

5. Data from the literature on the catalytic properties of alkalis are examined. It is suggested that alkaline catalysis is very widespread.

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2-AMINOVINYL KETONES

COMMUNICATION 5. ALKYLATION OF 2-DIALKYLAMINOVINYL KETONES. NEW SYNTHESIS OF HYDROXYMETHYLENE KETONES

N. K. Kochetkov, M. G. Ivanova, and A. N. Nesmeyanov

2-Dialkylaminovinyl ketones, which have become accessible owing to the development of a convenient method for their synthesis in our laboratory [1], are highly reactive and are of interest on account of their application in organic synthesis. One of us recently described the reaction of 4-dimethylamino-3-buten-2-one with methyl iodide [2]; this proceeds with transfer of the reaction center, and hydrolysis of the reaction product gives the hydroxymethylene ketone 4-hydroxy-3-methyl-3-buten-2-one:

$$CH_3COCH=CHN(CH_3)_2 + CH_3I \rightarrow CH_3COCH(CH_3)-CH=\overset{+}{N}(CH_3)_2I \xrightarrow{-H_2O} CH_3COC(CH_3)=CHOH + NH(CH_3)_2 \cdot HI.$$

Apart from its theoretical importance, this reaction is of interest from the preparative point of view, since it opens the way to the synthesis of hydroxymethylene ketones. Until now, hydroxymethylene ketones have been prepared exclusively by Claisen formylation of the corresponding ketones [3]. A disadvantage of this method is its equivocality, as a result of which either a mixture of the two possible formylation products is obtained [4], or the hydroxymethylene ketone obtained must be investigated in order to determine its structure, since the position at which the formylation of an unsymmetrical ketone will occur cannot always be predicted [5].

We have now made a more detailed study of the alkylation of 2-dialkylaminovinyl ketones, and we have also extended the method of preparation of the latter [1], particularly to the synthesis of aryl 2-dialkylaminovinyl ketones. Our study of the alkylation of alkyl 2-dimethylaminovinyl ketones with methyl iodide showed that the reaction is general and can form the basis of a new method of synthesizing hydroxymethylene ketones:

$$RCOCH=CHN(CH_3)_2 + CH_3I \rightarrow RCOCH(CH_3)-CH=\overset{+}{N}(CH_3)_2\bar{I} \xrightarrow{H_2O} RCOC(CH_3)=CHOH.$$

In this way we prepared the following hydroxymethylene ketones in 35-55% yield: 1-hydroxy-2-methyl-1--hexen-3-one, 1-hydroxy-2,5-dimethyl-1-hexen-3-one, and 1-hydroxy-2-methyl-1-octen-3-one. It was found that to obtain the most satisfactory result it is not necessary to isolate the intermediate alkylation product, as it was thought to be earlier [2]; it is better to submit the reaction mixture obtained in the alkylation directly to hydrolysis. It is better to carry out the alkylation itself at a high temperature, the mixture of the dialkylaminovinyl ketone and excess of methyl iodide being heated for several hours in autoclave at 100-110°. This gives higher yields than alkylation in boiling methyl iodide [2], for in the latter case the yields of hydromethylene ketones do not exceed 20%.

The hydroxymethylene ketones so obtained are colorless oils, which change slowly when kept. They give a violet color with ferric chloride and form crystalline complex copper salts, which can be used for their identification. In order to prove the structure of these compounds, one of them – 1-hydroxy-2,5-dimethyl-1-hexen--3-one – was hydrolyzed with hot dilute alkali. 5-Methyl-3-hexanone was isolated from the products and was identified by its semicarbazone; a calomel test showed the presence of formic acid in the reaction mixture:

$$(CH_3)_2CHCH_2\overset{\overset{CH_3}{|}}{C}OC{=}CHOH \xrightarrow[NaOH]{H_2O} (CH_3)_2CHCH_2COCH_2CH_3 + HCO_2H.$$

We studied also the possibility of alkylating dialkylaminovinyl ketones with other alkylating agents, but serious limitations were encountered. As we passed from methyl iodide to the higher alkyl halides, the yields of hydroxymethylene ketones fell off sharply. Thus, reaction of 1-dimethylamino-5-methyl-1-hexen-3-one with ethyl iodide gave 5-(hydroxymethylene-2-methyl-4-heptanone, but we could not obtain a yield of above 22%. When we passed to butyl iodide, the corresponding 5-(hydroxymethylene)-2-methyl-4-nonanone was not obtained in ananalytically pure state and the yield was less than 15%. Replacement of alkyl iodides by the corresponding bromides gave negative results. Dimethyl sulfate gave the corresponding hydroxymethylene ketone in 4-5% yield. Negative results were obtained also when dialkylaminovinyl ketones were treated with benzyl chloride, chlorotriphenylmethane, and 1-chloro-3-nitrobenzene. Nevertheless, our results are of interest, for, in spite of its limitations, the new method of synthesizing hydroxymethylene ketones has its advantages and it supplements the only other known method for synthesizing these important compounds.

EXPERIMENTAL

1-Dimethylamino-1-penten-3-one. This was prepared by the general method for the synthesis of alkyl 2-dialkylaminovinyl ketones [1], the reactants being 33.5 g of 1-chloro-1-penten-3-one and 73 ml of a 40% aqueous solution of dimethylamine. The yield was 20.2 g (56.4%). The substance has the following constants: b.p. 95-96° (4 mm); n_D^{20} 1.5400; d_4^{20} 0.9533; found MR 41.84; calculated MR 38.01.

Found %: N 11.45; 11.27. $C_7H_{13}ON$. Calculated %: N 11.01

1-Dimethylamino-1-penten-3-one is a colorless oil which can be preserved a long time without change.

1-Dimethylamino-1-octen-3-one. This was prepared similarly from 67 g of 1-chloro-1-octen-3-one and 120 g of a 40% aqueous solution of dimethylamine. The yield was 51 g (58%). The substance has the following constants: b.p. 157-158° (8 mm); n_D^{20} 1.5232; d_4^{20} 0.9213; found MR 58.14; calculated MR 51.86.

Found %: N 8.33; 8.48. $C_{10}H_{19}ON$. Calculated %: N 8.27

1-Dimethylamino-1-octen-3-one is a colorless oil which can be preserved a long time without change.

3-Dimethylaminoacrylophenone. This was prepared similarly from 34 g of 3-chloroacrylophenone [6] and 60 g of a 30% aqueous solution of dimethylamine. The crystalline substance that separated was filtered off and recrystallized from petroleum ether. The yield was 32 g (88%). 3-Dimethylaminoacrylophenone forms yellowish needles, m.p. 90-91° (the literature [7] gives 91-92°).

4'-Chloro-3-dimethylaminoacrylophenone. A solution of 11 g of 3,4'-dichloroacrylophenone [6] in 15 ml of benzene was added dropwise to 20 ml of a strongly cooled, vigorously stirred 30% aqueous solution of dimethylamine. The reaction mixture was stirred for one hour further, and the precipitate was filtered off and recrystallized from ligroin. The yield of yellowish needles, m.p. 85°, was 9.4 g (82.4%).

Found %: N 7.00; 7.11. $C_{11}H_{12}ONCl$. Calculated %: N 6.68.

The substance is readily soluble in the usual organic solvents, less readily soluble in ligroin, and insoluble in water.

1-Hydroxy-2-methyl-1-hexen-3-one. A mixture of 8 g of 1-dimethylamino-1-hexen-3-one [1] and 16 g of methyl iodide was heated for two hours at 110-120° in a small autoclave. The reaction product had the appearance of a brown resin. It was refluxed in a flask with twice its volume of water for two hours. When cool, the mixture was extracted with ether, the extract was dried over magnesium sulfate, solvent was distilled off, and the residue was vacuum distilled. A fraction of b.p. 65-67° (12 mm) was collected; yield 3.7 g (51%).

After being redistilled, the substance had the following constants: b.p. 63-65° (10 mm); n_D^{20} 1.4599; d_4^{20} 1.0002.

Found %: C 65.55; 65.49; H 9.80; 9.67. $C_7H_{12}O_2$. Calculated %: C 65.59; H 9.45.

1-Hydroxy-2-methyl-1-hexen-3-one is a colorless oil of feeble odor. It is insoluble in water, but dissolves in organic solvents. It darkens when kept for a long time. It gives a violet color with aqueous ferric chloride.

Copper salt. A few drops of 1-hydroxy-2-methyl-1-hexen-3-one was shaken with saturated aqueous cupric acetate. The fine dark-green precipitate was extracted with benzene, the extract was dried over sodium sulfate, benzene was evaporated off, and the residue was crystallized from absolute alcohol. Glistening dark-green crystals, m.p. 145°, were obtained.

Found %: C 53.25; H 6.96. $C_{14}H_{22}O_4Cu$. Calculated %: C 52.89; H 6.97.

1-Hydroxy-2,5-dimethyl-1-hexen-3-one. This was prepared similarly by heating 12 g of 1-dimethylamino--5-methyl-1-hexen-3-one [1] with 22 g of methyl iodide at 100-110° for three hours. The yield was 5.91 g (52%). The substance has the following constants: b.p. 66-68° (9 mm); n_D^{20} 1.4620; d_4^{20} 0.9467.

Found %: C 67.37; 67.49; H 10.24; 1026. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.92.

1-Hydroxy-2,5-dimethyl-1-hexen-3-one is a colorless oil of feeble odor. It is insoluble in water, but dissolves in organic solvents. It darkens when kept for a long time. It gives a violet color with aqueous ferric chloride.

The copper salt was prepared as before: glistening dark-green crystals, m.p. 161-162° (from absolute alcohol).

Found %: C 55.57; 55.62; H 7.60; 7.46. $C_{16}H_{26}O_4Cu$. Calculated %: C 55.55; H 7.45.

1-Hydroxy-2-methyl-1-octen-3-one. This was prepared similarly by heating 10 g of 1-dimethylamino--1-octen-3-one with 17 g of methyl iodide at 110-120° for two hours. The yield was 3.5 g (38%). The substance has the following constants: b.p. 99-101° (14 mm) n_D^{20} 1.4494; d_4^{20} 0.9428.

Found %: C 62.56; 62.61; H 10.42; 10.51. $C_9H_{16}O_2$. Calculated %: C 62.79; H 10.32.

1-Hydroxy-2-methyl-1-octen-3-one is a colorless oil of feeble odor. It darkens slowly when kept for a long time. It gives an intense violet color with aqueous ferric chloride.

The copper salt was prepared as before: glistening dark-green crystals, m.p. 115° (from absolute alcohol).

Found %: C 58.07; 58.26; H 8.25; 8.38. $C_{18}H_{34}O_4Cu$. Calculated %: C 57.80; H 8.09.

5-(Hydroxymethylene)-2-methyl-4-heptanone. This was prepared similarly by heating 10 g of 1-dimethylamino-5-methyl-1-hexen-3-one with 20 g of ethyl iodide at 110-120° for four hours. The yield was 2.2 g (22%). The substance has the following constants: b.p. 92-93° (9 mm); n_D^{20} 1.4570; d_4^{20} 0.9405.

Found %: C 62.47; 62.49; H 10.55; 10.59. $C_9H_{16}O_2$. Calculated %: C 62.79; H 10.32.

5-(Hydroxymethylene)-2-methyl-4-heptanone is a colorless oil of feeble odor. It darkens slowly when kept for a long time. It gives an intense violet color with aqueous ferric chloride.

Copper salt. A dark-green oil, insoluble in water, soluble in organic solvents.

Hydrolysis of 1-Hydroxy-2,5-dimethyl-1-hexen-3-one. A mixture of 5.2 g of 1-hydroxy-2,5-dimethyl--1-hexen-3-one and 250 ml of 5% aqueous caustic soda was prepared in a 500-ml distilling flask. The mixture was distilled slowly over a period of three hours, and a colorless oil having a pleasant camphorlike odor came over with the steam. The distillate was saturated with sodium chloride and extracted with ether. The extract was dried over sodium sulfate. Solvent was distilled off, and distillation of the residue gave 2.5 g (59%) of 5--methyl-3-hexanone, b.p. 134-136°; n_D^{20} 1.4064; d_4^{20} 0.8090; found MR 34.69; calculated MR 34.53. For 5--methyl-3-hexanone the literature [8] gives b.p. 134.5-135°; d_4^{20} 0.829.

Semicarbazone. This was prepared in the usual way: colorless crystals, m.p. 129-130° (from alcohol) (the literature [9] gives 129°).

Part of the aqueous alkaline solution remaining in the distilling flask was filtered, neutralized with concentrated hydrochloric acid, and rendered alkaline by addition of solid sodium carbonate. Addition of mercuric

chloride to this solution gave a precipitate of calomel (confirmed by reaction with ammonia).

SUMMARY

1. A study was made of the reaction of alkyl 2-dimethylaminovinyl ketones with methyl iodide; after hydrolysis of the reaction mixture, hydroxymethylene ketones are obtained. This reaction provides a new method for the synthesis of hydroxymethylene ketones.

2. It was shown that, with increase in the size of the alkyl radical of the alkylating agent, the alkylation of dimethylaminovinyl ketones becomes more difficult and the yields of hydroxymethylene ketones diminish.

3. The structure of the compounds obtained was proved by hydrolysis.

4. The method of synthesizing 2-dialkylaminovinyl ketones from 2-chlorovinyl ketones was extended to the synthesis of aryl 2-dialkylaminovinyl ketones.

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o-PHENYLENE ESTERS OF PYROPHOSPHOROUS ACID

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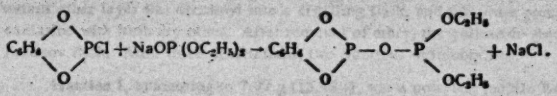
Esters of hypophosphoric and pyrophosphoric acids were first prepared in the chemically pure state by A. E. Arbuzov and B. A. Arbuzov [1] in 1932. By the method that they developed they succeeded in preparing pyrophosphorous esters. The present paper gives the results of experiments on the preparation of dialkyl o-phenylene pyrophosphites.

When an ethereal solution of o-phenylene phosphorochloridite [2] was treated with an ethereal solution of sodium diethyl phosphite in an atmosphere of dry nitrogen, reaction occurred with a slight evolution of heat and the separation of a white precipitate of sodium chloride. It was thought that reaction occurred in accordance with the following equation:

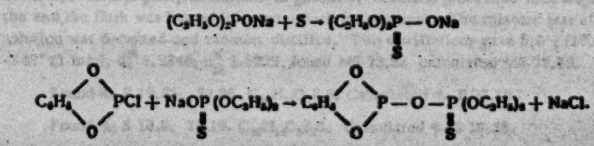


However, in the fractionation of the reaction products, instead of the single ester expected, two fractions were obtained: a liquid, and a crystalline solid.

Further investigation showed that the liquid fraction was diethyl o-phenylene pyrophosphite, a colorless liquid of characteristic odor: b.p. 115-116° (1 mm), d_4^{20} 1.1816; and n_D^{20} 1.4800. After being distilled, the second, high-boiling fraction rapidly crystallized in the receiver to a white mass, rapidly deliquescing in the air: b.p. 170-172° (1 mm), d_4^{20} 1.3107, and n_D^{20} 1.5502. We did not succeed in determining the melting point of the crystals, owing to their high hygroscopicity. The results for phosphorus analysis and molecular refraction indicated that the crystalline fraction was di-o-phenylene pyrophosphite. Hydrolysis of the ester with water in a sealed tube at 140° gave an almost theoretical yield of pyrocatechol. The yields of the esters, calculated on the amount of o-phenylene phosphorochloridite taken, were in neither case more than 14%. Replacement of o-phenylene phosphorochloridite by o-phenylene phosphorobromidite [3] did not affect the yields of these esters.

When diethyl o-phenylene pyrophosphite was treated with the calculated amount of cuprous chloride, bromide, or iodide, the temperature of the mixture rose to 58° and a honeylike mass was formed which we were unable to purify and analyze. When cuprous chloride, bromide, or iodide was mixed with di-o-phenylene pyrophosphite, the temperature of the mixture rose to 60° with formation at first of a honeylike mass, which cooled to a white solid mass that was either completely insoluble in the usual solvents, or soluble with decomposition.

Attempts to bring about the addition of sulfur to the two esters were not successful. The expected addition product from sulfur and diethyl o-phenylene pyrophosphite was prepared by another method, namely, by the reactions:



The product was a colorless liquid of unpleasant odor (not so unpleasant in the purified state), and it had the following constants: b.p. 145-147°, d_4^{20} 1.2846, and n_D^{20} 1.5229. Analyses for sulfur and phosphorus gave satisfactory results. When kept for a long time, even in sealed tubes, the liquid became yellow with simultaneous precipitation of sulfur.

When diethyl o-phenylene pyrophosphite was heated at 200° in sealed tubes with bromotriphenylmethane (an equimolecular amount), reaction occurred with separation of ethyl bromide. Hydrolisis of the reaction product with weak hydrochloric acid in sealed tubes at 200° for four hours gave triphenylmethylphosphonic acid and pyrocatechol.

EXPERIMENTAL

Preparation of Diethyl o-Phenylene Pyrophosphite and Di-o-phenylene Pyrophosphite

Dry ether (250 ml) and sodium wire (4.1 g) were placed in a three-necked flask fitted with mechanical stirrer, reflux condenser, and dropping funnel. An ethereal solution of 27 g of freshly distilled diethyl hydrogen phosphite was gradually added from the dropping funnel. When the whole of the sodium had reacted, dry nitrogen was passed, the mechanical stirrer was brought into operation, and an ethereal solution of 32 g of o-phenylene phosphorochloridite was added dropwise. After 4-5 minutes from the start of reaction, a white turbidity appeared and the temperature of the reaction mixture rose slightly. When reaction was complete, the contents of the reaction flask were heated in a water bath at the boiling point of ether for one hour. On the next day the supernatant ether layer was decanted into a distilling flask, and the white precipitate was washed three times by decantation with fresh dry ether. After removal of ether, the yellowish-green oil that remained was distilled from an Arbuzov flask. After three distillations, two fractions were obtained.

Fraction I, amounting to 7.02 g (13.79%), was a colorless mobile liquid having b.p. 115-116° (1 mm), d_4^{20} 1.1816, n_D^{20} 1.4800, found MR 66.78, calculated MR 67.17.

Found %: P 22.83; 22.11. $C_{18}H_{14}O_5P_2$. Calculated %: P 22.46.

Fraction II, amounting to 7.5 g (14.8%), had the following constants: b.p. 170-172° (1 mm), d_4^{20} 1.3107, n_D^{20} 1.5502, found MR 71.47, calculated MR 71.07.

Found %: P 20.96; 20.63. $C_{12}H_8O_5P_2$. Calculated %: P 21.08.

Hydrolysis of 1.05 g of Fraction II in a sealed tube at 140° gave 0.6 g of a crystalline substance, m.p. 103° (pyrocatechol melts at 104°; the amount of pyrocatechol calculated for $C_{12}H_8O_5P_2$ is 0.78 g).

The experiment was repeated under the same conditions but with o-phenylene phosphorobromidite in place of o-phenylene phosphorochloridite. The same yields of the same fractions were obtained.

Action of Bromotriphenylmethane on Diethyl o-Phenylene Pyrophosphite

When 1 g of diethyl o-phenylene pyrophosphite was heated with 1.17 g of bromotriphenylmethane in a sealed tube at 170-175° and the product was hydrolyzed with weak hydrochloric acid, triphenylmethylphosphonic acid was obtained; after recrystallization from alcohol it melted at 276°. Removal of water from the aqueous solution gave crystals of pyrocatechol, which melted at 101° after recrystallization from benzene.

Preparation of Diethyl o-Phenylene Thionohypophosphate

o-Phenylene phosphorochloridite (31 g) was added carefully to a solution of the calculated amount of sodium O,O-diethyl phosphorothioate in gasoline. Reaction proceeded with slight evolution of heat, and toward the end the flask was heated in a water bath for one hour. The mixture was allowed to settle, and the gasoline solution was decanted and vacuum distilled. Two distillations gave 5.8 g (10.6%) of a fraction having b.p. 145-147° (1 mm), d_4^{20} 1.2846, n_D^{20} 1.5229, found MR 73.22, calculated MR 72.89.

Found %: P 19.65; 20.28. $C_{18}H_{14}O_5P_2S$. Calculated %: P 20.12.

Found %: S 10.6; 10.19. $C_{18}H_{14}O_5P_2S$. Calculated %: S 10.38.

SUMMARY

1. Diethyl o-phenylene pyrophosphite and di-o-phenylene pyrophosphite were prepared and their properties were studied.

2. Diethyl o-phenylene thionohypophosphate was prepared.

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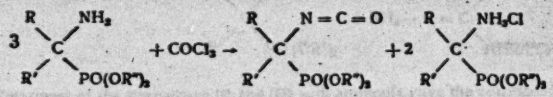
DERIVATIVES OF 1-AMINOALKYLPHOSPHONIC ACIDS.

1-ISOCYANATOALKYLPHOSPHONIC ESTERS AND THEIR REACTIONS

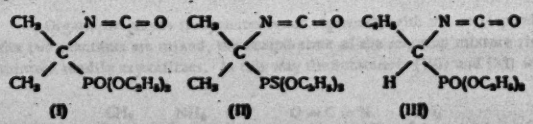
T. Ya. Medved and M. I. Kabachnik

Study of the properties of aminoalkylphosphonic and aminoalkylphosphonothionic acids and their derivatives has shown that substances of this type are capable of various types of reactions associated with the presence of a free amino group. One or both of the hydrogens of the amino group may be alkylated [1]; exhaustive methylation of these compounds gives the corresponding "phosphonobetaines" [2]; treatment with acid anhydrides and chlorides gives N-acyl derivatives [3]; reaction with chloroformic esters gives organophosphorus urethans [4]; reaction with aryl isocyanates gives organophosphorus urea derivatives [5].

In the present paper we describe organophosphorus isocyanates prepared by the action of phosgene on aminoalkylphosphonic and aminoalkylphosphonothionic esters:

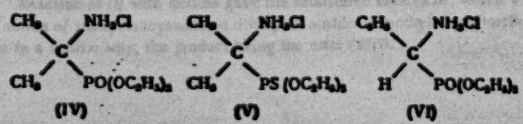


Reaction is very vigorous: it is most convenient to carry the reaction out in toluene solution at not above 0° with a considerable excess of phosgene. The reaction was carried out with diethyl esters of 1-amino-1-methylethylphosphonic, 1-amino-1-methylethylphosphonothionic, and α-aminobenzylphosphonic acids. The products were the corresponding organophosphoric isocyanates: diethyl 1-isocyanato-1-methylethylphosphonate (I), O,O-diethyl 1-isocyanato-1-methylethylphosphonothioate (II), and diethyl α-isocyanatobenzylphosphonate (III):



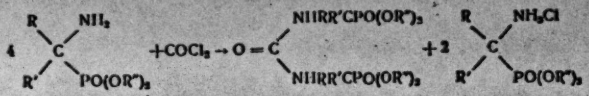
(I) (II) (III)

The yields of these were 96%, 68%, and 38% respectively. These substances are colorless mobile liquids, readily soluble in organic solvents and decomposed by water. The hydrochlorides of the original substances (IV, V, and VI), which were formed simultaneously, were also isolated and characterized. We have prepared (VI) previously[6].



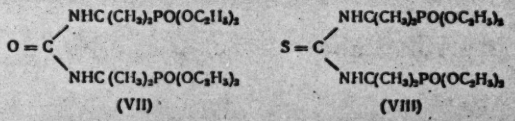
(IV) (V) (VI)

When the reaction was carried out with the calculated amount of phosgene, organophosphorus urea derivatives were obtained:

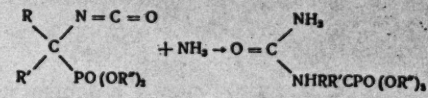


Thus, treatment of diethyl 1-amino-1-methylethylphosphonate with phosgene gave the substance (VII).

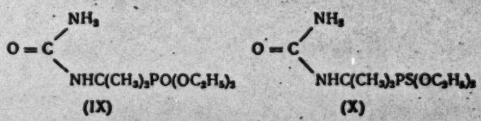
The analogous derivative of thiourea (VIII) was prepared by reaction between the same ester and carbon disulfide.



Like other isocyanates, the organophosphorus isocyanates that we have prepared readily react with amines and alcohols. By reaction with ammonia in ethereal solution at room temperature, high yields are obtained of monosubstituted organophosphorus ureas:

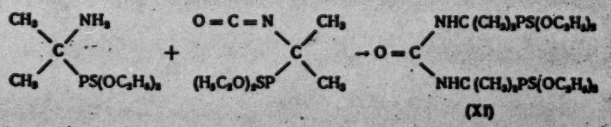


Treatment of the isocyanates (I) and (II) with ammonia gave the corresponding ureidoalkylphosphonic esters (IX) and (X):

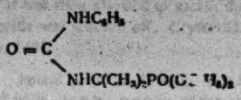


These are colorless crystalline substances, readily soluble in water and alcohol.

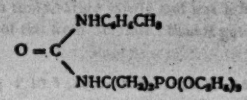
Organophosphorus isocyanates react vigorously with the corresponding organophosphorus amines. When the two reactants are mixed, the temperature of the reaction mixture rises rapidly; when cool, the reaction mixture readily crystallizes. In this way the Substances (VII) and (XI) were prepared.



Reaction of (I) with aniline gave the substituted urea (XII), which we had synthesized previously [5] by the action of phenyl isocyanate on diethyl 1-amino-1-methylethylphosphonate. Reaction with p-toluidine went in a similar way, the product being the ester (XIII).

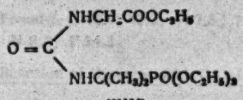


(XII)

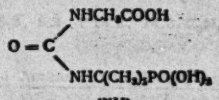


(XIII)

Reaction of the isocyanate (I) with glycine ethyl ester gave the Compound (XIV), and hydrolysis of this product with hydrochloric acid gave the tribasic acid (XV).

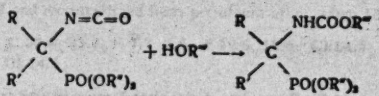


(XIV)



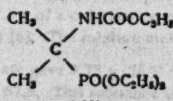
(XV)

Reaction of the organophosphorus isocyanates with alcohols gave the corresponding urethans:

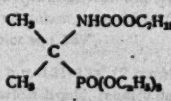


Reaction with ethanol proceeds readily when the reactants were simply mixed together, and to complete it 10-15 minutes in a boiling water bath is sufficient. The urethan (XVI) so obtained was synthesized by us previously [4] by the action of ethyl chloroformate on diethyl 1-amino-1-methylethylphosphonate.

In the reaction with heptyl alcohol [synthesis of (XVII)], it is necessary to heat the mixture in a boiling water bath for one hour in presence of trimethylamine as catalyst.

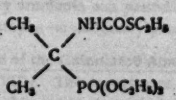


(XVI)

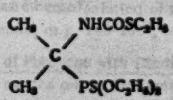


(XVII)

Ethanethiol reacts only in presence of a catalyst (trimethylamine), and it is necessary to heat the reaction mixture in a sealed tube in a boiling water bath for a long time. In this way the thiourethans (XVIII) and (XIX) were prepared.



(XVIII)



(XIX)

EXPERIMENTAL

Reaction of phosgene with Diethyl 1-Amino-1-methylethylphosphonate [Synthesis of (I) and (IV)]. A solution of 19 g (0.19 mole) of phosgene in 40 ml of toluene was placed in a round-bottomed flask fitted with stirrer, dropping funnel, thermometer, and reflux condenser. The solution was cooled to a temperature of from −4 to −5°, and was stirred while a solution of 14.7 g (0.075 mole) of diethyl 1-amino-1-methylethylphosphonate in 15 ml of toluene was added. Addition was continued for about one hour, the temperature of the mixture

being maintained in the range 0 to −5°. The mixture was stirred at the same temperature for about four hours, and it was then allowed to attain the room temperature slowly and was left overnight. The precipitated hydrochloride was filtered off. Crystallization of this from absolute ethanol gave 9.7 g of colorless crystals of (IV), m.p. 140°.

Found %: C 36.6, 36.8; H 8.5, 8.4; P 13.5, 13.5; N 6.1, 5.9; Cl 15.3, 15.5. $C_7H_{19}PNO_3Cl$. Calculated %: C 36.3; H 8.3; P 13.4; N 6.1; Cl 15.3.

Phosgene and toluene were distilled from the filtrate under reduced pressure, and the residue was vacuum distilled. Two distillations gave 5.4 g (96%) of (I), b.p. 75-77° (3 mm); n_D^{20} 1.4349; d_4^{20} 1.1014; found MR 52.4, calculated MR 52.7. The ester (I) is a colorless mobile liquid, soluble in organic solvents and slowly decomposed by water.

Found %: C 42.9, 43.2; H 7.5, 7.5; N 6.2, 6.2; P 14.2, 14.2. $C_8H_{16}PO_4N$. Calculated %: C 43.4; H 7.3; N 6.3; P 14.1.

Reaction of Phosgene with O,O-Diethyl 1-Amino-1-methylethylphosphonothioate [Synthesis of (II) and (V)]. The procedure was as above, reaction being between 37 g (0.37 mole) of phosgene in 60 ml of toluene and 31.7 g (0.15 mole) of 0,0-diethyl 1-amino-1-methylethylphosphonothioate in 10 milliliters of toluene. When reaction was complete the mixture remained colorless and clear. Phosgene and toluene were distilled off under reduced pressure. When cooled with an ice-salt mixture, the residue crystallized partially. The crystals were filtered off and recrystallized from petroleum ether, when 18 g of (V), m.p. 108°, was obtained.

Found %: C 33.8, 33.8; H 7.7, 7.6; P 12.6, 12.5; Cl 14.5, 14.4. $C_7H_{15}NPO_2SCL$. Calculated %: C 33.9; H 7.7; P 12.5; Cl 14.3.

The filtrate was vacuum fractionated, and two distillations gave 8.1 g (68%) of (II), b.p. 71-74° (3 mm); n_D^{20} 1.4778; d_4^{20} 1.1102; found MR 60.5; calculated MR 60.2. This compound is a colorless mobile liquid, readily decomposed by water. It has good solubility in organic solvents.

Found %: P 13.3, 13.3. $C_8H_{16}NPO_2S$. Calculated %: P 13.1.

Reaction of Phosgene with Diethyl α-Aminobenzylphosphonate [Synthesis of (III) and (VI)]. Reaction was between 11 g (0.11 mole) of phosgene in 40 ml of toluene and 5.5 g (0.022 mole) of diethyl α-aminobenzylphosphonate in 6 ml of toluene. The precipitated hydrochloride was filtered off. Recrystallization of this from ethanol gave 7.5 g of a colorless crystalline substance, m.p. 157-158° (VI). This substance has been characterized previously [6]. The mixture melting point was 157°.

The filtrate gave 0.72 g (36%) of (III), b.p. 131-134° (2 mm); n_D^{20} 1.5052; d_4^{20} 1.1825; found MR 67.5; calculated MR 67.6. This substance is a colorless liquid, readily decomposed by water, and soluble in organic solvents.

Found %: C 54.1, 54.0; H 5.9, 6.1; P 11.3, 11.4; N 4.8, 4.9. $C_{12}H_{18}NPO_4$. Calculated %: C 53.3; H 6.0; P 11.5; N 5.2.

When dry ammonia was passed into an ethereal solution of the substance, a colorless crystalline precipitate of diethyl α-ureidobenzylphosphonate, m.p. 148-150°, was obtained.

Reaction of the Calculated Amount of Phosgene with Diethyl 1-Amino-1-methylethylphosphonate [Synthesis of (VII)]. The experiment was carried out in the same apparatus. A solution of 9.8 g (0.05 mole) of diethyl 1-amino-1-methylethylphosphonate was cooled to 0° in the flask, and a solution of 1.25 g (0.0125 mole) of phosgene in 4 ml of toluene was added gradually. The temperature of the reaction mixture was maintained in the range 0-5°. The reaction mixture was then stirred for about one hour at 20°, after which the precipitate present was filtered off and recrystallized from absolute ethanol. Colorless crystals (3.3 g) of the salt (IV), m.p. 140°, were obtained. From the filtrate remaining after the removal of the precipitate, phosgene and toluene were distilled off. On the next day the residue crystallized. Three recrystallizations from petroleum ether gave 1 g (20%) of colorless needles, m.p. 72-73°.

Found %: C 43.3, 43.6; H 8.4, 8.4; P 14.9, 15.0; N 6.7, 6.8; $C_{15}H_{34}N_2P_2O_7$. Calculated %: C 43.3; H 8.3; P 14.9; N 6.7.

The substance is soluble in water, alcohol, ether, benzene, and other organic solvents.

Reaction of Carbon Disulfide with Diethyl 1-Amino-1-methylethylphosphonate [Synthesis of (VIII)]. A mixture of 7.8 g (0.04 mole) of diethyl 1-amino-1-methylethlphosphonate, 4.5 g (0.06 mole) of carbon disulfide, and 10 ml of ether was prepared in a flask having a ground-in stopper. The mixture was allowed to stand at room temperature, and after two weeks the precipitate was filtered off and washed with ether. Crystallization from absolute alcohol gave 1.6 g of a colorless crystalline substance, m.p. 273-274°.

Found %: C 36.4, 36.5; H 8.3, 8.5; N 8.4, 8.2; P 18.5, 18.3. $C_5H_{14}NPO_3$. Calculated %: C 35.9; N 8.4; N 8.4; P 18.5.

The analysis corresponded to ethyl hydrogen 1-amino-1-methylethylphosphonate. After it had stood for a further two weeks, the filtrate - a thick sirupy liquid - crystallized. Washing the crystals with ether gave 2.3 g (25%) of the product, m.p. 97-98°.

Found %: C 41.6, 41.6; H 7.8, N 6.5, 6.4; S 7.6, 7.6. $C_{15}H_{32}N_2P_2O_6S$. Calculated %: C 41.6; H 7.9; N 6.5; S 7.4.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Ammonia [Synthesis of (IX)]. Dry ammonia was passed through a solution of 0.7 g of the isocyanate (I) in 7 ml of ether cooled to 0°. Filtration gave 0.65 g (86%) of colorless crystals, m.p. 138-139°.

Found %: C 39.9, 39.9; H 8.1, 8.0; P 13.0, 13.2; N 11.8, 11.9. $C_5H_{13}PN_2O_4$. Calculated %: C 40.3; H 8.1; P 13.1; N 11.8.

The substance is readily soluble in water and alcohol, but is insoluble in diethyl ether and in petroleum ether.

Reaction of O,O-Diethyl 1-Isocyanato-1-methylethylphosphonothioate with Ammonia [Synthesis of (X)]. Reaction was carried out as in the preceding experiment with 1 g of the isocyanate (II) and dry ammonia. On reduction to one-third bulk by evaporation of ether, a white crystalline precipitate was formed. The product, which amounted to 0.6 g (61%), melted at 104-106°.

Found %: C 37.9, 38.1; H 7.6, 7.6; N 10.9, 11.0; P 11.9, 11.9; S 12.2, 12.2. $C_5H_{13}N_2PO_3S$. Calculated %: C 37.8; H 7.6; N 11.0; P 12.2; S 12.6.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Diethyl 1-Amino-1-methylethylphosphonate [Synthesis of (VII)]. To 0.33 g (0.0017 mole) of diethyl 1-amino-1-methylethylphosphonate, 0.46 g (0.0021 mole) of the isocyanate (I) was added; the temperature of the mixture rose to 45°. The mixture was heated for three minutes in a boiling water bath. After being cooled with an ice-salt mixture and rubbed out with a glass rod, the mixture crystallized. Recrystallization from petroleum ether gave 0.5 g (71.5%) of colorless crystals, m.p. 73-74°. A mixture with the substance obtained in the reaction with phosgene melted at the same temperature.

Reaction of O,O-Diethyl 1-Isocyanato-1-methylethylphosphonothioate with O,O-Diethyl 1-Amino-1-methylphosphonothioate [Synthesis of (XI)]. Reaction was carried out as in the preceding experiment, the reactants being 2.1 g (0.01 mole) of O,O-diethyl 1-amino-1-methylethylphosphonothioate and 3 g (0.0125 mole) of the isocyanate (II). Recrystallization from a small amount of petroleum ether gave 2.8 g (62%) of a colorless substance, m.p. 72-73°.

Found %: C 40.2, 40.2; H 7.7, 7.7; S 13.6, 13.6; P 13.4, 13.7; N 6.2, 6.1. $C_{12}H_{32}N_2P_2S_2O_5$ Calculated %: C 40.2; H 7.7; S 14.3; P 13.8; N 6.3.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Aniline [Synthesis of (XII)]. Reaction was carried out as in the preceding experiment, the reactants being 0.6 g (0.0065 mole) of aniline and 1.1 g (0.005 mole) of the isocyanate (I). The crystals were washed with petroleum ether and recrystallized from absolute ethanol. The yield of the colorless crystalline product, m.p. 137-138°, was 1.1 g (73%). The same substance, prepared previously [3] by the action of phenyl isocyanate on diethyl 1-amino-1-methylethylphosphonate, melted at 139-140°. The mixture melting point was 138°.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with p-Toluidine [Synthesis of (XIII)]. To 0.70 g (0.0065 mole) of p-toluidine in 1 ml of ether, 1.1 g (0.005 mole) of the isocyanate (I) was added. The temperature of the mixture rose from 20° to 27°, and the reaction mixture solidified. The substance was washed with petroleum ether and recrystallized from absolute ethanol. The yield of colorless crystals, m.p. 157-158° was 1.1 g (68%).

Found %: C 54.8, 54.9; H 7.8, 7.7; P 9.3, 9.1; N 8.4, 8.3. $C_{15}H_{23}N_2PO_4$. Calculated %: C 54.9; H 7.7; P 9.4; N 8.5.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Glycine Ethyl Ester [Synthesis of (XIV)]. When 4.22 g (0.019 mole) of the isocyanate (I) was added to 2.1 g (0.02 mole) of glycine ethyl ester, the temperature rose to 105°. When cool, the mixture crystallized. The substance was washed with petroleum ether and recrystallized from a mixture of absolute ethanol and petroleum ether. The product, amounting to 5.9 g (96%), melted at 82-83°.

Found %: N 8.4, 8.4; P 9.6, 9.5. $C_{11}H_{21}N_2PO_6$. Calculated %: N 8.6; P 9.6.

Hydrolysis of the Ester (XIV) with Hydrochloric Acid. A mixture of 2 g of the substance obtained in the preceding experiment and 50 ml of 1:1 hydrochloric acid was refluxed for 4.5 hours. Hydrochloric acid was distilled off under reduced pressure, and the dry residue was recrystallized from water. The product (0.6 g) formed colorless crystals, m.p. 127-128°; it crystallized with one molecule of water.

Found %: C 27.8, 27.9; H 6.1, 5.9; N 10.8, 10.6. $C_8H_{13}N_2PO_6 \cdot H_2O$. Calculated %: C 27.9; H 5.9; N 10.8.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Ethanol [Synthesis of (XVI)]. The isocyanate (I) (1.1 g) was added to 5 ml of absolute ethanol; the temperature of the mixture rose from 20° to 25°. The mixture was then heated for 15 minutes in a boiling water bath. Excess of alcohol was distilled off, and vacuum distillation of the residue gave 0.77 g (58%) of a colorless mobile liquid, b.p. 110-111° (2 mm) and n_D^{20} 1.4508. As prepared previously by us [4], this substance had b.p. 110-112° (2 mm) n_D^{20} 1.4519.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Heptyl Alcohol [Synthesis of (XVII)]. A mixture of 2.2 g of the isocyanate (I), 3.5 g of heptyl alcohol, and 0.5 ml of an ethereal solution of trimethylamine was heated for one hour in a boiling water bath. Excess of the alcohol was distilled off. Vacuum distillation of the residue gave 2.1 g (62%) of a fraction having b.p. 158-159° (2 mm); n_D^{20} 1.4517; d_4^{20} 1.0351; found MR 87.8; calculated MR 87.6.

Found %: C 53.4, 53.3; H 9.7, 9.6; P 9.0, 9.0. $C_{13}H_{28}PO_5N$. Calculated %: C 53.4; H 9.6; P 9.2.

Reaction of Diethyl 1-Isocyanato-1-methylethylphosphonate with Ethanethiol [Synthesis of (XVIII)]. A mixture of 5 g of the isocyanate (I), 7 g of ethanethiol, and 1.0 ml of ethereal trimethylamine was heated in a sealed tube for eight hours in a boiling water bath. When excess of ethanethiol had been distilled off, the residue in the flask crystallized. Recrystallization of the substance from petroleum ether gave 3 g (47%) of colorless crystals, m.p. 64-65°.

Found %: C 42.0, 42.3; H 7.7, 7.6; S 11.3, 11.2; P 10.4, 10.3; N 4.8, 4.7. $C_{10}H_{22}NPSO_4$. Calculated %: C 42.4; H 7.8; S 11.3; P 10.9; N 4.9.

The substance is readily soluble in water, alcohol, benzene, and other organic solvents.

Reaction of O,O-Diethyl 1-Isocyanato-1-methylethylphosphonothioate with Ethanethiol [Synthesis of (XIX)]. A mixture of 5 g of the isocyanate (II), 6.5 g of ethanethiol, and 1.0 ml of ethereal trimethylamine was heated in a sealed glass tube for eight hours in a boiling water bath. Excess of ethanethiol was distilled off. Vacuum distillation of the residue gave 3.1 g (50%) of a fraction of b.p. 132-133° (3 mm); n_D^{20} 1.5075; d_4^{20} 1.1361; found MR 78.5, calculated MR 78.4.

Found %: C 39.6, 39.6; H 7.3, 7.2; P 10.8, 10.8; N 4.5, 4.3. $C_{10}H_{22}NPS_2O_3$. Calculated %: C 40.1; H 7.4; P 10.3; N 4.7.

SUMMARY

1. 1-Isocyanatoalkylphosphonic esters were synthesized, and their reactions were studied.

2. It was shown that 1-aminoalkylphosphonic esters (1-amino-1-methylethylphosphonic, 1-amino-1-methylethylphosphonothionic, and α-aminobenzylphosphonic esters) react with phosgene and, depending on the conditions, the corresponding isocyanates or symmetrical substituted ureas are formed.

3. 1-Isocyanatoalkylphosphonic esters react with ammonia to give the corresponding unsymmetrical ureas, with alcohols to give urethans, with amines to give substituted ureas, and with thiols to give thiourethans.

4. Treatment of a 1-amino-1-methylethylphosphonic ester with carbon disulfide gives a disubstituted thiourea.

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*T.p. = C. B. Translation pagination.

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ORGANOBORON COMPOUNDS

COMMUNICATION 10. COMPLEX NATURE OF SALTS OF ORGANOBORON ACIDS

B. M. Mikhailov, T. K. Kozminskaya, A. N. Blokhina, and T. A. Shchegoleva

One of us, in collaboration with Vaver [1], recently prepared salts derived from diphenylborinic acid which contained quadricovalent negatively charged boron (I):

$$[(C_6H_5)_2B(OH)_2]M,$$

$$M = Na, K, NH_4. \qquad (I)$$

This observation prompted us to investigate the nature of the salts of other organoboron acids and so determine whether the complex structure of salts of diphenylborinic acid is due to peculiarities in the structure of the acid itself, or is possessed also by other organoboron acids, e.g. boronic acids $RB(OH)_2$.

Michaelis and Becker [2] carried out an investigation on salt formation in the areneboronic acid series, and they considered that benzeneboronic acid forms a normal salt of composition $C_6H_5B(ONa)_2$ with caustic soda and an acid salt $(C_6H_5BO_2H)_2Ca$ with calcium hydroxide. The investigation that we have now carried out has shown that Michaelis and Becker were wrong in considering the salts of benzeneboronic acid to be tercovalent boron derivatives. We found that, when equimolecular amounts of benzeneboronic acid and caustic soda were mixed in aqueous solution and the mixture was evaporated to dryness, crystallization of the residue from a mixture of benzene and methanol gave a sodium salt corresponding in composition to the complex salt sodium trihydroxy (phenyl) borate (II)•:

$$[C_6H_5B(OH)_3]Na \qquad (II)$$

When benzeneboronic acid and caustic soda were mixed in aqueous solution in the proportions of 1 : 2, the same complex salt (II) was obtained, and not the normal salt $C_6H_5B(ONa)_2$. The residue remaining after the evaporation of the aqueous solution of the original acid and caustic soda was not a homogeneous substance, but appeared to be a mixture of caustic soda and sodium trihydroxy(phenyl)borate (II). In this case the isolation of the salt (II) was more difficult, for its solubility in various solvents is similar to that of caustic soda. Nevertheless, by repeated crystallization we succeeded in obtaining the salt (II) in an analytically pure state. Michaelis and Becker did not crystallize the product obtained by the evaporation of an aqueous solution of the acid and caustic soda taken in the proportions of 1:2, but submitted it directly to analysis.

The calcium salt formed by benzeneboronic acid was prepared by boiling an aqueous-alcoholic solution of the acid with calcium hydroxide and evaporating the resulting solution. The analysis of the recrystallized salt corresponded to calcium trihydroxy(phenyl)borate [(III), M = Ca]:

$$[C_6H_5B(OH)_3]_2M. \qquad (III)$$

• As there is no recognized system of nomenclature for these complex salts, they are named by an adaptation of the nomenclature of coordinate compounds, "organic" names, however, being given to radicals (e.g. hydroxy, not hydroxo). The authors' name for the acid $[C_6H_5B(OH)_3]H$ may be transcribed as phenylboronic acid; they regard it as a derivative of $[B(OH)_4]H$, their name for which may be transcribed as boronic acid. — Publisher.

When the calcium salt (III) was treated with carbon dioxide, benzeneboronic acid was obtained, and Michaelis and Becker, in treating the aqueous solution of the reactants with carbon dioxide, could not possibly have obtained calcium benzeneboronate. The barium salt, obtained by the action of barium hydroxide on benzeneboronic acid, was found to have the same structure as the calcium salt [(III), M = Ba].

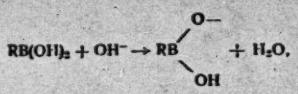
Apart from salts derived from benzeneboronic acid, we studied the alkali-metal salts formed by o-toluene-, p-bromobenzene-, p-anisole-, and 1-naphthalene-boronic acids. The salts derived from these acids were prepared similarly to those derived from benzeneboronic acid and were purified by crystallization. Like the salts derived from benzeneboronic acid, they were all found to be complex trihydroxy(phenyl)borates (IV):

$$[ArB(OH)_3]M$$
$$Ar = p\text{-}CH_3C_6H_4-,\ p\text{-}CH_3OC_6H_4-,\ p\text{-}BrC_6H_4-,$$
$$1\text{-}C_{10}H_7-;\ M = Na, K. \qquad (IV)$$

Among the salts of alkaneboronic acids, the literature describes the sodium salt of 1-butaneboronic acid; this is assigned the structure of an acid salt containing one-half of a molecule of water of crystallization, $n\text{-}C_4H_9BO_2HNa \cdot 1/2H_2O$ [3]. Actually, the sodium salt derived from 1-butaneboronic acid is quite different in composition and structure. In fact, like the salts derived from areneboronic acids, it is derived from a complex acid – butyltrihydroxyboric acid and has the structure (V):

$$[n\text{-}C_4H_9B(OH)_3]Na. \qquad (V)$$

It follows from these considerations that, in reactions with bases, organoboron acids do not behave as hydrogen acids, i.e. as proton donors, as was universally believed:



but as acceptors of hydroxyl ions:

$$RB(OH)_2 + OH^- \rightarrow [RB(OH)_3]^-.$$

The salts so formed are complex compounds containing quadricovalent negatively charged boron.

EXPERIMENTAL

The salts were analyzed by Wittig's method [4]. The content of alkali or alkaline-earth metal was determined by the titration of aqueous or aqueous-alcoholic solutions of the salts with acid in presence of bromocresol purple. In the determination of boron, the boric acid formed by decomposing the salt with mercuric chloride was titrated in presence of mannitol. After treatment with mercuric chloride, the solution of the salt had a neutral reaction, which indicated that equivalent amounts of aryl groups and metal were present.

1. Sodium Trihydroxy(phenyl)borate

a) A solution of 1.22 g (0.01 mole) of benzeneboronic acid in 5 ml of 2 N NaOH (0.01 mole) was prepared and filtered. It was evaporated down under reduced pressure with exclusion of carbon dioxide. Crystallization of the residue from a mixture of methanol and benzene gave fine needles of the salt.

Found %: Na 14.06, 14.05; B 6.47. $[C_6H_5B(OH)_3]Na$. Calculated %: Na 14.20; B 6.68.

b) A solution of 1.83 g (0.015 mole) of benzeneboronic acid in 15 ml of 2 N NaOH (0.03 mole) was evaporated to dryness. The residue was crystallized twice from a mixture of water (7 ml) and acetone (50 ml), and then from a mixture of methanol (2.5 ml) and benzene (40 ml). The product weighed 1.5 g.

Found %: Na 13.92, 14.12. $C_6H_5B(OH)_3Na$. Calculated %: Na 14.20. $C_6H_5B(ONa)_2$. Calculated %: Na 27.72.

2. Calcium Trihydroxy(phenyl)borate

A stirred mixture of 2.44 g (0.02 mole) of benzeneboronic acid, 0.8 g (0.01 mole) of calcium hydroxide, 120 ml of water, and 60 ml of methanol was boiled for three hours. The hot solution was filtered and evaporated to dryness. The residue was crystallized from a mixture of water (100 ml) and acetone (100 ml).

Found %: Ca 12.47, 12.71; B 6.64. $[C_6H_5B(OH)_3]_2Ca$. Calculated %: Ca 12.58; B 6.80.

A solution of 1.3 g of the calcium trihydroxy(phenyl)borate so obtained in 100 ml of a 1 : 1 mixture of water and methanol was saturated with carbon dioxide. The precipitate (0.35 g) did not contain any organic matter. The filtrate was evaporated to dryness, and 0.83 g of benzeneboronic acid, m.p. 214-216°, was obtained.

3. Barium Trihydroxy(phenyl)borate

A mixture of 1 g (0.008 mole) of benzeneboronic acid, 1.3 g (0.004 mole) of $Ba(OH)_2 \cdot 8H_2O$, and 25 ml of water was boiled for 15 minutes. The warm solution was filtered, and the filtrate was concentrated under reduced pressure (with exclusion of carbon dioxide) in a water bath until the volume was reduced to 10 ml. The barium salt, which separated in the form of six-sided plates, was analyzed for barium content by heating an aqueous solution of the salt for 14 minutes with excess of acid and back-titrating the acid that did not react.

Found %: Ba 32.74; B 5.23. $[C_6H_5B(OH)_3]_2Ba$. Calculated %: Ba 33.07; B 5.21.

4. Sodium Trihydroxy(p-methoxyphenyl)borate

A solution of 1 g (0.0066 mole) of p-anisoleboronic acid in N NaOH (0.0066 mole) was filtered and evaporated to dryness. The residue was crystallized from a mixture of water (10 ml) and acetone (40 ml).

Found %: Na 12.11, 12.09; Ba 5.56; 5.66. $CH_3OC_6H_4B(OH)_3Na$. Calculated %: Na 12.00; Ba 5.63.

5. Sodium (p-Bromophenyl)trihydroxyborate

A solution of 2 g (0.01 mole) of p-bromobenzeneboronic acid in N NaOH (0.01 mole) was filtered and evaporated to dryness. Crystallization of the residue from a methanol-benzene mixture gave fine needles of the salt.

Found %: Na 9.45, 9.37; B 4.31, 4.41 $[BrC_6H_4B(OH)_3]Na$. Calculated %: Na 9.55; B 4.49.

6. Potassium (p-Bromophenyl)trihydroxyborate

The salt was prepared under the conditions described above.

Found %: K 15.20, 15.14; B 4.08, 4.21. $[BrC_6H_4B(OH)_3]K$. Calculated %: K 15.22; B 4.21.

7. Sodium Trihydroxy-o-tolylborate

The salt was prepared under the conditions described above.

Found %: Na 13.24, 13.20; B 5.98, 6.07. $[CH_3C_6H_4B(OH)_3]Na$. Calculated %: Na 13.07; B 6.14.

8. Sodium Trihydroxy-1-naphthylborate

The salt was prepared under the conditions described above.

Found %: Na 10.64, 10.45; B 5.02, 5.15. $[C_{10}H_7B(OH)_3]Na$. Calculated %: Na 10.84; B 5.10.

9. Sodium Butyltrihydroxyborate

Saturated caustic soda solution (30-40 ml) was added to a solution prepared by dissolving 2 g (0.02 mole) of 1-butaneboronic acid in 10 ml of 20% caustic soda solution. The precipitate then formed was filtered off, dried in the air, and dissolved in 20 ml of absolute alcohol. The solution was filtered and 100 ml of acetone was added. The salt that separated was filtered off, washed with ether, and dried in a vacuum desiccator.

Found %: Na 16.22, 16.19; B 7.58, 7.66. $[C_4H_9B(OH)_3]Na$. Calculated %: Na 16.21; B 7.52.

SUMMARY

Contrary to general belief, in reactions with bases organoboron acids do not behave as hydrogen acids, i.e. as proton donors, but as acceptors of hydroxyl ions. The resulting salts are complex compounds containquadricovalent negatively charged boron, e.g. $[RB(OH)_3]M$.

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ACTION OF ACTIVE NITROGEN ON ORGANIC SUBSTANCES

COMMUNICATION 2

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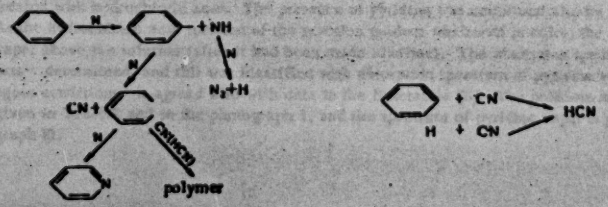
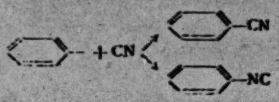
In Communication 1 [1] we described the action of active nitrogen on some organic compounds and showed that aromatic hydrocarbons form hydrogen cyanide and a solid polymeric substance. In a further study of the reaction of active nitrogen with benzene we have succeeded in isolating and identifying three further reaction products: phenyl isocyanide, benzonitrile, and pyridine. The formation of the first two substances was suggested a long time ago [2] on the basis of the odor of the reaction mixture, but the presence of pyridine among the reaction products was unexpected. The formation of this substance could be explained on the assumption that on colliding with nitrogen atoms the benzene molecule suffers severe breakdown with formation of fragments containing one or two carbon atoms; these particles (molecules or radicals) then react with hydrogen cyanide with formation of pyridine, just as pyridine is formed from acetylene and hydrogen cyanide. If this assumption is correct, then treatment of other aromatic hydrocarbons, e.g. naphthalene, with active nitrogen should also give pyridine, but spectroscopic investigation of the products of reaction between active nitrogen and naphthalene showed that pyridine was absent, whereas quinoline and isoquinoline were shown to be present.

Our results and previous observations enable us to advance certain views concerning the mechanism of reaction between active nitrogen and aromatic hydrocarbons. In the reaction vessel there is an intense violet glow, characteristic of the CN radical [3], and hydrogen cyanide, with only traces of cyanogen, can be detected in the reaction products [1]; we may therefore suppose that at first CN radicals are formed, and later these are converted into hydrogen cyanide. The formation of hydrogen cyanide may result from the capture of a hydrogen from the aromatic nucleus, and also from combination of the CN radical with atomic hydrogen, the presence of which in the reaction mixture was proved by the formation of stearic from oleic acid [1] and of saturated from unsaturated hydrocarbons [4].

In the primary collision between a nitrogen atom and a benzene molecule, the radicals C_6H_5 and NH are probably formed. By reacting further with active nitrogen, the NH radical will give a nitrogen molecule and a hydrogen atom. The further action of nitrogen on the phenyl radical will give a CN radical and a C_5H_5 residue. When this C_5H_5 radical collides with a nitrogen atom, pyridine will be formed, but as the life of a C_5H_5 radical must be extremely short, the probability of the formation of pyridine will be extremely low. The C_5H_5 radical will generally decompose further with formation of unsaturated compounds or the corresponding radicals, which will copolymerize with the CN radical or hydrogen cyanide, the polymer so formed being deposited on the walls of the reaction vessel.

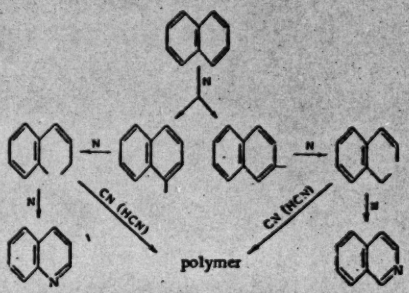


Formation of phenyl isocyanide and benzonitrile evidently results from collisions between phenyl and CN radicals:



It might be supposed also that NH radicals formed as a result of the primary collision between nitrogen atoms and benzene would react with hydrogen atoms and phenyl radicals (in either order) with formation of aniline, but no aniline could be detected in the reaction mixture.

The course of the reaction between naphthalene and active nitrogen is probably similar to that of the reaction with benzene. The nitrogen can attack either an α- or a β- position, and the naphthyl radicals formed will again react with nitrogen with formation of CN radicals and C_9H_7 residues. By further reaction with nitrogen these residues will give quinoline and isoquinoline:



No naphthylamines were detected among the products of reaction between active nitrogen and naphthalene.

In the investigation of the products of reaction between active nitrogen and benzene, the presence of phenyl isocyanide was proved by its hydrolysis to aniline, which was converted into a dye by diazotization and coupling with 2-naphthol. This reaction provided a proof of the presence of phenyl isocyanide only with it was certain that no aniline was present in the reaction mixture. The detection of aniline in presence of phenyl isocyanide is difficult, owing to the readiness with which the latter is hydrolyzed. Hence, in order to remove phenyl isocyanide, the mixture was first treated with mercuric chloride [5], after which it was shown that aniline was absent. The possibility of the detection of aniline under these conditions was first checked on an artificial mixture of phenyl isocyanide, aniline, and benzene. An attempt was made to apply the reaction with mercuric chloride for the determination of the phenyl isocyanide content of the mixture, the amount of calomel formed being measured. However, experiments on pure phenyl isocyanide gave nonreproducible results. The absence of aniline was confirmed also by spectroscopic determinations. The presence of benzonitrile among the reaction products was proved by the isolation of benzoic acid by alkaline hydrolysis; a substance that was probably terephthalic acid was also isolated.

Pyridine was isolated as a complex compound with mercuric chloride after the reaction products had been treated with hydrochloric acid. The presence of pyridine was confirmed also by spectroscopic measurements. As the hydrochloric acid solution of the reaction product was brown in color, the spectrum was determined on the vapor above the solution (after it had been made alkaline). The absorption spectrum over the range 2000-2800 A was determined, and this was identified with absorption spectrum of pyridine vapor determined under analogous conditions; it agreed also with data in the literature [6]. The positions and character of the bands are given in Table 1 and in the photograph 1, and the spectrum of pyridine vapor is given for comparison (photograph 2).

TABLE 1

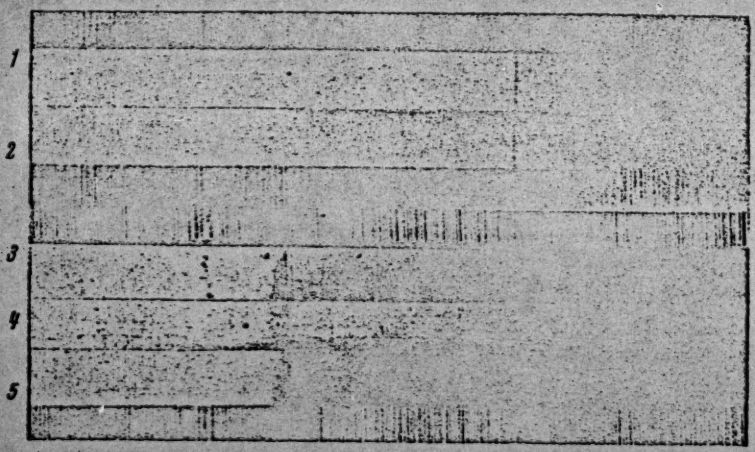
Asorption Spectrum of the Vapor of the Products of Reaction Between Active Nitrogen and Benzene

Band No.	λ (A)	ν̃ (cm⁻¹)	Intensity (visual)	Character of band
1	2875.3	34769	7	
2	2863.8	34908	4	
3	2847.0	35114	3	
4	2831.2	35310	9	
5	2820.8	35441	4	
6	2805.5	35634	6	
7	2796.1	35754	3	
8	2788.2	35885	10	
9	2780.5	35954	3	Diffuse
10	2763.2	36174	4	Diffuse
11	2753.5	36307	5	Diffuse
12	2747.2	36390	3	"
13	2719.1	36766	3	"
14	2713.1	36847	2	"

TABLE 2

Asorption Spectrum of the Vapor of the Products of Reaction Between Active Nitrogen and Naphthalene

Band No.	λ (A)	ν̃ (cm⁻¹)	Intensity (visual)	Character of band
1	3139.1	31847	3	
2	3135.5	31884	6	
3	3131.3	31926	10	
4	3126.0	31981	8	
5	3108.0	32166	2	Broad, diffuse
6	3082.0	32437	4	
7	3063.2	32636	2	
8	3058.4	32687	6	
9	3053.6	32739	1	Diffuse, broad
10	3046	32820	3	
11	3035.2	32937	3	Diffuse
12	3007	33246	2	
13	2976	33592	2	Diffuse, broad
14	2953	33854	1	Diffuse



1) Absorption spectrum of the vapor of the products of reaction between active nitrogen and benzene; 2) spectrum of pyridine vapor; 3) absorption spectrum of isoquinline vapor; 4) absorption spectrum of the vapor of the products of reaction between active nitrogen and naphthalene; 5) absorption spectrum of quinoline vapor.

Owing to the low yield of products in the reaction between active nitrogen and naphthalene, it was found difficult to identify them by chemical methods. We therefore determined the absorption spectrum of the vapor of the reaction products. The spectrum was distributed over the region 3200-2900 A. The positions and character of the bands are given in Table 2 and in the photograph 4.

The spectrum obtained was compared with the absorption spectra of quinoline [7] and isoquinoline vapors. As there are no data in the literature on the absorption spectrum of isoquinoline vapor, this spectrum was determined under conditions analogous to those used for the spectrum of the vapors of the reaction products, the same spectrograph being employed. The form of the spectrum of isoquinoline vapor, which occurs in the range 3250-2900 A, and the character of the bands are given in Table 3 and in the photograph 3.

TABLE 3

Absorption Spectrum of Isoquinoline Vapor

Band No.	λ (A)	ν (cm⁻¹)	Intensity (visual)	Character of band
1	3210	31144	4	Diffuse, breadth 20 A
2	3143.2	31806	2	
3	3139.1	31847	3	
4	3135.6	31883	6	
5	3131.3	31926	10	
6	3126.0	31981	8	
7	3082.0	32437	4	
8	3063.4	32634	2	
9	3058.3	32688	6	
10	3053.8	32737	1	
11	3035.2	32938	3	Diffuse
12	3018	33125	2	
13	2998	33346	4	Diffuse, broad
14	2976	33592	1	Diffuse

The spectrum of quinoline vapor is given for comparison in the photograph 5. The most intense bands in the spectra of the reaction products were those attributable to isoquinoline.

It may be assumed that more isoquinoline than quinoline is formed in the reaction between active nitrogen and naphthalene, for in the spectra of the solutions quinoline and isoquinoline [8] absorb to approximately the same extent.

EXPERIMENTAL

Experiments with benzene. The reaction between benzene and active nitrogen was carried out in a tube or in a sphere (see Communication 1). The p.d. across the electrodes of the discharge tube was 2200-2300 V, the current strength was 150-160 ma, and the pressure was 10 mm. The reaction products were allowed to accumulate for 25-50 hours. Volatile reaction products were distilled from the contents of the traps (which had been cooled with liquid nitrogen), and the residue was a brown liquid which contained some dark-colored flakes and possessed the sharp odor of an isocyanide. At the end of an experiment of 5-7 hours, the mixture was poured into a flask, and the trap was washed with 2-3 ml of benzene, which was added to the bulk of the mixture. The further treatment of the mixture was carried out in different ways, depending on the object in view.

Determination of aniline. The mixture obtained in the traps in the course of a six-hour experiment was filtered, and 3 ml of a 20% solution of mercuric chloride in absolute alcohol was added to the filtrate. The reaction products obtained on subsequent days (in the course of 25 hours, in all) were also filtered, and the filtrates were added to the mixture containing mercuric chloride. The resulting mixture was a brown liquid containing a light-colored flocculent precipitate. It smelled of bitter almonds, no isocyanide odor being detected. Solvents were distilled off under reduced pressure, and the residue was boiled with 20 ml of 5% hydrochloric acid in order to dissolve the complex compound of aniline and mercuric chloride. The mixture was cooled and filtered, and two drops of 0.05 N nitrite solution were added to the filtrate. There was no coloration when the solution was tested with alkaline 2-naphthol solution.

In order to verify the method of detecting aniline in presence of phenyl isocyanide, 1 ml of a 50% benzene solution of pheayl isocyanide (prepared according to Nef's instructions [9] was mixed with 1 ml of a 2% benzene solution of aniline, and 3 ml of benzene and 1 ml of a 20% solution of mercuric chloride in absolute alcohol were added. The solvents were distilled off, and the residue was boiled with 20 ml of 5% hydrochloric acid.

The mixture was cooled and filtered, and a drop of sodium nitrite solution was added to the filtrate. There was a distinct orange-red coloration when alkaline 2-naphthol solution was added.

Determination of phenyl isocyanide and benzonitrile. At the end of each one-day experiment, the contents of the traps were boiled with 1 ml of 10% hydrochloric acid for 15 minutes in order to hydrolyze the phenyl isocyanide. When the products of reaction for 50 hours – all treated in the same way – had accumulated, the mixture was filtered, and the benzene layer was separated from the aqueous layer.

a) The benzene layer was a light-brown liquid smelling of bitter almonds. After removal of solvent, 120 mg of a mixture of brown oil and crystals was obtained. Alcohol (2 ml) was added to the mixture, and the very small white precipitate was filtered off. Aqueous caustic potash (1 ml of 50%) was added to the alcoholic solution, and the mixture was boiled for two hours, by which time the almond odor had disappeared. The mixture was diluted with 3 ml of water and washed with ether. The aqueous layer was acidified with hydrochloric acid, and the precipitate that formed was extracted with ether (only a part). The residue (15 mg) was filtered off, washed; it sublimed without melting and was soluble in sodium carbonate solution with formation of a brown solution having a bright blue fluorescence. A low-melting gray powder (60 mg) was isolated from the ether solution, and three crystallizations of this from water gave 10 mg of white crystals, m.p. 119-120°; in admixture with benzoic acid it melted at 120-120.5°.

b) The aqueous layer, which was also brown, was titrated under ice cooling with 0.1 N sodium nitrite: 2.72 ml, corresponding to 25.3 mg of aniline, was required. The solution obtained gave an orange-red precipitate with alkaline 2-naphthol solution.

Determination of pyridine. The mixture from the traps was treated as in the determination of phenyl isocyanide and benzonitrile. When the aqueous layer was made alkaline, a pyridine odor appeared. Pyridine was determined in the aqueous layer by two methods.

a) A hot solution of 0.8 g of mercuric chloride in 8 ml of water was added to the hydrochloric acid solution. The mixture was cooled, and gray precipitate present was filtered off, washed with 1 ml of water, and dried in the air. The precipitate (100 mg) melted at 146-165°. After three crystallizations from water it melted at 173-176°. In admixture with $C_5H_5N \cdot HCl \cdot 2HgCl_2$ (m.p. 176-178°) it melted at 174-177°.

b) In the spectrometric determination of pyridine, a hydrochloric acid solution of the reaction products was poured in a thin layer on to the bottom of a quartz tube in the ends of which there were fused-in plane quartz windows. Excess of aqueous alkali was added through a side tube provided with a tap, so that gas was evolved from the solution and filled the tube. The absorption spectrum of the vapor in the tube (length of absorbing layer 17 cm) was determined at room temperature on a Q-12 quartz spectrograph. The light source was a superhigh-pressure krypton-filled lamp, which gave a continuous spectrum in the near ultraviolet. An iron-arc spectrum was used for comparison.

Experiments with naphthalene. The reaction of active nitrogen with naphthalene was carried out in a sphere. The naphthalene was poured directly into the reaction space, and active nitrogen was passed over its surface at a pressure of 13 mm. The p.d. applied to the electrodes of the discharge tube was 2800 V, and the current strength was 200 ma. Owing to the low vapor pressure of naphthalene, reaction was slow at room temperature, and the reaction was therefore carried out at 35-40°, at which temperature the vapor pressure of naphthalene approaches 1 mm.

The reaction products in the traps formed a dark-colored deposit, which was washed out with benzene. The resulting solution was extracted with hydrochloric acid, and the hydrochloric acid solution was filtered and then poured in a thin layer on to the bottom of a quartz tube having plane quartz windows, in which the spectrum was determined; the solution was made alkaline and the absorption spectrum of the vapor of the reaction products was determined on a 17-cm layer with the same spectrograph. The spectrum was determined at 20° and 90°, and the results obtained at 90° are shown in Table 2.

In conclusion we express our deep indebtedness to I. V. Obreimov for his advice and constant interest in our work. We thank also V. I. Dianov-Klokov for designing the apparatus for the preparation of active nitrogen.

SUMMARY

1. In the reaction between active nitrogen and benzene, the products include not only hydrogen cyanide and a deposit on the walls of the reaction vessel, but also small amounts of pyridine, phenyl isocyanide,

benzonitrile, and probably terephthalonitrile. It was shown that quinoline and isoquinoline are present among the products of reaction between active nitrogen and naphthalene.

2. Some views are expressed on the possible mechanism of the reaction between active nitrogen and aromatic hydrocarbons.

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SYNTHESIS OF ALKOXY- AND ACETOXY-SILANES CONTAINING AN ETHER OR ESTER GROUPING SUBSTITUTED IN SILICON-ATTACHED ALKYL

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A few alkoxysilanes containing an ether or ester grouping substituted in silicon-attached alkyl are known, but they have received very little study. Some compounds of this type containing an ether grouping were prepared by reaction between alkoxy(chloroalkyl)silanes and a sodium alkoxide in an alcohol medium [1]. Compounds containing an ester grouping were prepared by reaction of (chloromethyl)diethoxymethylsilane with sodiomalonic and sodioacetoacetic esters [2]. Addition of chlorodimethylsilane at the double-bond of undecenoic esters and subsequent replacement of silicon-attached chlorine by ethoxyl gave compounds containing an ester grouping at the end of a silicon-attached chain of eleven carbon atoms [3]. No acetoxysilanes containing an ester grouping in a silicon-attached alkyl have been described. The synthesis of alkoxy- and acetoxy-silanes containing ether and ester groupings is of interest in that these compounds can form the basis of a study of the effect of ether and ester groupings on the stability of the C—Si bond in presence of nucleophilic and other reagents.

In the present investigation, alkoxy- and acetoxy-silanes containing an ether or ester grouping substituted in silicon-containing alkyl were synthesized, namely:

$RSiX(OC_2H_5)_2$, $XSi(OCOCH_3)_3$, and $RSiX(OCOCH_3)_2$, in which R = Alk or Ar, and X = CH_2OR, $CH_2COOC_2H_5$, or CH_2OCOCH_3.

(Alkoxymethyl)alkyldiethoxysilanes were synthesized as follows:

a) $ClCH_2SiCl_2(CH_3) + 2C_2H_5OH \rightarrow ClCH_2Si(OC_2H_5)_2(CH_3) + 2HCl$,

b) $ClCH_2Si(OC_2H_5)_2(CH_3) + C_2H_5ONa \rightarrow C_2H_5OCH_2Si(OC_2H_5)_2(CH_3) + NaCl$.

Alkyl- and aryl-diethoxy(ethoxycarbonylmethyl)silanes were synthesized as follows. An alkyl- or aryltrichlorosilane was first treated with alcohol:

a) $RSiCl_3 + 2C_2H_5OH \rightarrow RSiCl(OC_2H_5)_2 + 2HCl$,

and the alkyl- or aryl-chlorodiethoxysilane was treated with sodium and ethyl bromoacetate:

b) $RSiCl(OC_2H_5)_2 + 2Na + BrCH_2COOC_2H_5 \rightarrow R{-}Si(CH_2COOC_2H_5)(OC_2H_5)_2 + NaCl + NaBr$

Acetoxy(acetoxymethyl)silanes were synthesized as follows:

TABLE

No.	Substance	Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
						Found	Calculated
1	Diethoxy(ethoxycarbonylmethyl) ethylsilane	$C_2H_5-Si(OC_2H_5)_2-CH_2COOC_2H_5$	149—150 (normal pressure)	1,4008	0,9080	62,60	61,35
2	Diethoxy(ethoxycarbonylmethyl) phenylsilane	$C_6H_5-Si(OC_2H_5)_2-CH_2COOC_2H_5$	106—112 (7)	1,4600	1,0080	72,62	72,16
3	Diacetoxy(acetoxymethyl)methylsilane	$CH_3-Si(OCOCH_3)_2-CH_2OCOCH_3$	90—95 (20)	1,4321	1,1529	52,65	52,00
4	Triacetoxy(acetoxymethyl)silane	$CH_3OCOCH_2-Si-(OCOCH_3)_3$	79—82 (10) (m.p. 70°)	—	—	—	—
5	Diethoxy(ethoxymethyl)methylsilane	$CH_3-Si(OC_2H_5)_2-CH_2OC_2H_5$	148—150 (normal pressure)	1,4120	0,9189	52,0	52,00
6	Diethoxy(methoxymethyl)methylsilane	$CH_3-Si(OC_2H_5)_2-CH_2OCH_3$	139—141	1,4088	0,9233	47,64	47,32

a) $ClCH_2SiCl_2 + 3ClCH_2COOK \rightarrow CH_3OCOCH_2Si(OCOCH_2)_3 + 3KCl;$

b) $ClCH_2SiCl_3 + 4ClCH_2COOK \rightarrow CH_3OCOCH_2{\cdot}Si(OCOCH_2)_3 + 4KCl.$

The properties of the new compounds obtained by the above reactions are given in the table.

EXPERIMENTAL

1. Synthesis of Diethoxy(ethoxycarbonylmethyl)ethylsilane

a) Synthesis of Chlorodiethoxyethylsilane. The reaction was carried out in a three-necked flask fitted with stirrer, reflux condenser, dropping funnel, and thermometer. Absolute ethanol (184.0 g) was added dropwise to 327 g of trichloroethylsilane (b.p. 98°; chlorine content 63.7%); during the addition, the temperature fell to 5°. When the whole of the alcohol had been added, the mixture was heated at 70-80° for 15 hours. The product was distilled from a flask fitted with a fractionating column, 200 mm in length. The product, which amounted to 274 g (75%), came over at 140-144°.

b) Synthesis of Diethoxy(ethoxycarbonylmethyl)ethylsilane. The synthesis was carried out in a three-necked flask fitted with stirrer, dropping funnel, reflux condenser, and thermometer. Sodium (23 g) was heated with xylene in a round-bottomed flask until the xylene boiled. The flask was then closed and shaken vigorously, so that the molten sodium became finely divided. The xylene standing over the sodium was replaced by ether, and the sodium was then transferred to the reaction flask and covered with ether (100 g). The mixture was stirred, and a mixture of 91.3 g of chlorodiethoxyethylsilane and 83.5 g of ethyl bromoacetate was added dropwise. Reaction occurred with evolution of heat, and the rate at which the mixture was added was regulated so that the ether in the reaction flask boiled regularly and gently. When the addition was complete, the reaction mixture was heated at 38-40° for 13 hours. The voluminous precipitate was filtered off (weight 110 g). The filtrate was distilled from a flask through a column: b.p. 149-150°; d_4^{20} 0.9080; n_D^{20} 1.4008; found MR 62.6; calculated MR 61.35

Found %: C 52.14; H 10.12; Si 11.0. $C_{10}H_{22}O_4Si$. Calculated%: C 51.28; H 9.40; Si 11.97.

2. Synthesis of Diethoxy(ethoxycarbonylmethyl)phenylsilane

a) Preparation of Chlorodiethoxyphenylsilane. Absolute ethanol (92 g) was added dropwise to 211.4 g of trichlorophenylsilane (b.p. 202°, chlorine content 49.8%) contained in a three-necked flask fitted with stirrer, dropping funnel, reflux condenser, and thermometer. When the whole of the alcohol had been added, the mixture was heated at 70-80° for 12 hours. Vacuum distillation gave 146.5 g (63.5%) of product, b.p. 92-93° (4 mm), chlorine content 15.03% (theory requires 15.4%).

b) Synthesis of Diethoxy(ethoxycarbonylmethyl)phenylsilane. The procedure was similar to that used in the synthesis of diethoxy(ethoxycarbonylmethyl)ethylsilane. The reactants were sodium (13.8 g), chlorodiethoxyphenylsilane (70 g), and ethyl bromoacetate (50.1 g). The precipitate formed was filtered off, and vacuum distillation of the filtrate gave 21.8 g (33.2%) of diethoxy(ethoxycarbonylmethyl)phenylsilane, b.p. 106-112° (7 mm); d_4^{20} 1.0080; n_D^{20} 1.4600; found MR 72.62; calculated MR 72.16

Found %: C 59.56; H 8.00; Si 10.04. $C_{14}H_{22}O_4Si$. Calculated %: C 59.57; H 7.80; Si 9.92.

3. Synthesis of Diethoxy(ethoxymethyl)methylsilane

a) Synthesis of (Chloromethyl)diethoxymethylsilane. Absolute ethanol (95 g) was added dropwise to 163.5 g of dichloro(chloromethyl)methylsilane contained in a three-necked flask fitted with stirrer, dropping funnel, reflux condenser, and thermometer. The temperature of the reaction mixture fell to 5°. When the whole of the alcohol had been added, the reaction mixture was heated at 70-80° until the evolution of hydrogen chloride ceased (20 hours). The product was distilled from a flask fitted with a Vigreux column. The yield of (chloromethyl)diethoxymethylsilane was 130 g (71.4%); it had b.p. 161-163°, n_D^{20} 1.4117; and chlorine content 19.9% (theory requires 19.4%).

b) Synthesis of Diethoxy(ethoxymethyl)methylsilane. The synthesis was in the same reaction flask. Sodium ethoxide was prepared by adding absolute ethanol (45 g) to finely divided sodium (13.8 g) in xylene (75 g). When the whole of the alcohol had been added, the mixture was heated at 70-80° for one hour. The mixture was cooled, and 113.8 g of (chloromethyl) diethoxymethylsilane was added dropwise, after which the mixture was heated at 70-80° for 12 hours. The voluminous precipitate was filtered off. Distillation of the filtrate through a Vigreux column gave 29.8 g (25.7%) of product, b.p. 148-150°; d_4^{20} 0.9189; n_D^{20} 1.4125; found MR 52.0; calculated MR 52.09.

Found %: C 49.83; H 9.83; Si 14.03. $C_8H_{20}O_3Si$. Calculated %: C 50.00; H 10.41; Si 14.58.

4. Synthesis of Diethoxy(methoxymethyl)methylsilane

The procedure was similar, but toluene was used as solvent. The substances taken in the reaction were sodium (6.9 g), methanol (20.0 g), (chloromethyl)diethoxymethylsilane (54.6 g), and toluene (50 g). Distillation of the filtrate through a column gave 15.8 g (29.5%) of product, b.p. 140-143°; d_4^{20} 0.9233; n_D^{20} 1.4088; found MR 47.64; calculated MR 47.32.

Found %: C 48.63; H 9.62; Si 14.15. $C_7H_{18}O_3Si$. Calculated %: C 47.19; H 10.11; Si 15.73.

5. Synthesis of Diacetoxy(acetoxymethyl)methylsilane

Dichloro(chloromethyl)methylsilane (81.7 g; b.p. 121-124°) was added dropwise to a mixture of 147 g of anhydrous potassium acetate and 200 g of toluene contained in a three-necked flask fitted with stirrer, dropping funnel, reflux condenser, and thermometer. During the addition the temperature of the mixture rose to 60°. When the whole of the silane had been added, the mixture was heated at 90-100° for 20 hours. The precipitate present was then filtered off, and vacuum distillation of the filtrate gave 43.4 g (36.7%) of diacetoxy(acetoxymethyl)methylsilane, b.p. 90-95° (20 mm); d_4^{20} 1.1529; n_D^{20} 1.4321; found MR 52.65; calculated MR 52.09.

Found %: C 41.76; H 6.04; Si 11.49; CH_3COO^- 49.63. $C_8H_{14}O_6Si$. Calculated %: C 41.02; H 5.10; Si 11.50; CH_3COO^- 50.04.

6. Synthesis of Triacetoxy(acetoxymethyl)silane

Trichloro(chloromethyl)silane (42.6 g) was added dropwise to a mixture of 117.8 g of anhydrous potassium acetate and 135 ml of toluene contained in a flask fitted with stirrer, dropping funnel, reflux condenser, and thermometer. During the addition the temperature of the mixture rose to 100°. When the addition was complete, the mixture was heated at 100-110° for 18 hours. The precipitate was then filtered off through a Buchner funnel, and the filtrate was vacuum distilled. The yield of triacetoxy(acetoxymethyl)silane was 21 g (25%); it was obtained in the form of crystals, m.p. 79.5°, b.p. 79-82° (10 mm).

Found %: C 38.14; H 4.90; Si 11.52. $C_9H_{14}O_8Si$. Calculated %: C 38.8; H 5.03; Si 10.0.

SUMMARY

1. An investigation was made into methods for the introduction of a silicon-attached alkyl containing an ether or ester grouping into certain alkoxyalkyl(or aryl)silanes and acetoxyalkylsilanes.

2. By the reaction of sodium and ethyl bromoacetate with chlorodiethoxyethylsilane and with chlorodiethoxyphenylsilane, the following organosilicon compounds were prepared for the first time: diethoxy-(ethoxycarbonylmethyl)ethylsilane and diethoxy(ethoxycarbonylmethyl)phenylsilane.

3. Reaction between alkoxy(chloroalkyl)silanes and sodium alkoxides yielded two new compounds: diethoxy(ethoxymethyl)methylsilane and diethoxy(metnoxymethyl)methylsilane.

4. Reaction between chloro(chloroalkyl)silanes and potassium acetate yielded two new compounds containing an acetoxy group in a silicon-attached alkyl radical: diacetoxy(acetoxymethyl)methylsilane and triacetoxy(acetoxymethyl)silane.

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SYNTHESIS AND REACTIONS OF ORGANOSILICON THIOCYANATES AND THIOLS

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We have already [1] reported the synthesis of the first two organosilicon thiocyanates in which the thiocyanato group is attached to carbon in the α-position with respect to silicon*. These organosilicon α thiocyanates, $(CH_3)_3SiCH_2SCN$ and $(C_2H_5)_2CH_3SiCH_2SCN$ were readily obtained by boiling the corresponding α-chloro compounds with ammonium thiocyanate in an acetone medium:

$$R_3SiCH_2Cl + NH_4SCN \rightarrow R_3SiCH_2SCN. \quad (1)$$

We now report the synthesis of some new α-thiocyanates by the aid of Reaction (1), and also the synthesis of the first α,α'-dithiocyanates and γ-thiocyanates by the Reactions (2), (3), and (4):

$$(CH_3)_2Si(CH_2Cl)_2 + 2NaSCN \rightarrow (CH_3)_2Si(CH_2SCN)_2. \quad (2)$$

$$[ClCH_2(CH_3)_2Si]_2O + 2NaSCN \rightarrow O[Si(CH_3)_2CH_2SCN]_2. \quad (3)$$

$$(CH_3)_3SiCH_2CH_2CH_2Cl + NaSCN \rightarrow (CH_3)_3SiCH_2CH_2CH_2SCN. \quad (4)$$

It was found that 96% ethanol was a better medium than acetone for the synthesis of the organosilicon thiocyanates, for its use enabled us to reduce the reaction volume considerably. It was shown also that in the Reactions (1)-(4), not only ammonium thiocyanate, but also potassium and sodium thiocyanates could be used, and the use of the last two salts resulted in higher yields of α-thiocyanates, even in an acetone medium. The introduction of these modifications into the original procedure enabled us to increase the yield, for example of $(CH_3)_3SiCH_2SCN$ and $(C_2H_5)_2CH_3SiCH_2SCN$, from 50% [1] to 85%. Finally, it was found that reaction between (iodomethyl)trimethylsilane and ammonium thiocyanate in an acetone medium gave $(CH_3)_3SiCH_2SCN$ in 80% yield, whereas Reaction (1), in which (chloromethyl)trimethylsilane was used, gave only a 50% yield of the α-thiocyanate [1].

The rate at which α-thiocyanates are formed in Reaction (1) is greatly reduced by substitution of the methyl radicals attached to silicon by ethyl, propyl, butyl, etc. The formation of the secondary α-thiocyanate $(CH_3)_2SiCH(SCN)CH_3$ is still more difficult. In these cases it is necessary to increase the duration of boiling greatly in order to increase the yields of organosilicon α-thiocyanates. This behavior is in accord with recent results [3] on the rate of ion exchange of the iodine in trialkyl(1-iodoalkyl)silanes, which was found to depend on the character of the radical attached to silicon.

In order to prove that the products of Reactions (1)-(4) were indeed thiocyanates (and not isothiocyanates, which are formed when alkyl- and aryl-chlorosilanes are treated with thiocyanate salts [4]:

$$R_3SiCl + NaSCN \rightarrow R_3SiNCS),$$

we studied the action of Grignard reagents on our products. It is known [5] that with thiocyanates RMgX forms thiols and sulfides, whereas with isothiocyanates it gives thiocarboxylic amides. As we had supposed [5], our products were thiocyanates, for with n-C_3H_7MgBr they gave the corresponding thiols in admixture with sulfides:

$$R_3SiCH_2SCN + n\text{-}C_3H_7MgX \rightarrow R_3SiCH_2SH + R_3SiCH_2SC_3H_7. \quad (5)$$

The synthesis of organosilicon thiols in which the thiol group was on the α-carbon was effected recently by the action of KHS [6] or thiourea [6,7] on the corresponding α-chloro compounds; in the second case the

* Cooper [2] has recently reported the synthesis of three organosilicon α-thiocyanates.

TABLE 1

No.	Organosilicon thiocyanate	Duration of boil (hours)	Medium	Cation M of MSCN	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated [12]	Found % C	Found % H	Found % Si	Found % S	Calculated % C	Calculated % H	Calculated % Si	Calculated % S
1	$(CH_3)_3SiCH_2SCN$	10	Alcohol	Na	84	198.5(750)	1.4682	0.9476	42.63	42.64	41.60 41.40	7.44 7.67	19.32 19.31	22.30 22.02	41.34	7.63	19.31	22.07
2	$(C_6H_5)_2CH_2SiCH_2SCN$	35	»	Na	88.5	72.5(2)	1.4778	0.9480	51.08	51.66	48.77 48.70	8.03 8.56	10.51 10.41	18.39 18.18	48.50	8.72	10.70	18.49
3	$(n\text{-}C_6H_7)_2CH_2SiCH_2SCN$	70	Acetone	Na	60	84—86(2)	1.4700	0.0289	61.14	61.16	53.57 53.50	9.02 9.53	14.15 14.13	15.77 16.05	53.67	9.51	13.93	15.02
4	$(n\text{-}C_6H_7)_3SiCH_2SCN$	45	»	NH_4	11.6	120(2)	1.4781	0.0247	70.24	70.42	56.96 57.19	10.03 10.00	12.27 12.18	13.00 13.88	57.58	10.10	12.23	13.97
5	$(n\text{-}C_6H_4)_2CH_2SiCH_2SCN$	105	»	Na	65.6	106.5(2)	1.4755	0.9174	70.26	70.42	56.75 56.91	9.90 10.11	12.67 12.47	13.48 13.60	57.58	10.10	12.23	13.97
6	$(C_6H_5)_3CH_2SiCH_2SCN$	26	Alcohol	Na	59.5	172(2)	1.5987	1.1204	82.11	82.28	67.09 66.95	5.07 5.61	10.15 10.28	11.94 12.03	66.88	5.61	10.41	11.90
7	$(CH_3)_2SiCH(SCN)CH_3$	137	Acetone	NH_4	9.3	123(5)	1.4702	0.9330	47.30	47.27	45.29 45.35	8.33 8.33	17.67 17.42	19.80 20.06	45.23	8.22	17.61	20.12
8	$(CH_3)_2Si(CH_2SCN)_2$	11	Alcohol	Na	70	142.5(2)	1.5361	1.1513	54.84	55.00	35.00 35.65	5.02 5.01	13.70 13.61	31.99 31.57	35.61	4.98	13.86	31.68
9	$[(CH_3)_2SiCH_2SCN]_2O$	35	Acetone	Na	52.5	148(2)	1.4942	1.0949	73.54	73.64	34.63 34.80	5.76 5.82	19.05 20.35	23.59 23.35	34.75	5.83	20.29	23.19
10	$(CH_3)_2SiCH_2CH_2CH_2SCN$	52	Alcohol	Na	71.5	66.8(1)	1.4685	0.9278	52.07	51.90	48.40 48.56	8.49 8.75	16.43 16.27	18.52 18.01	48.50	8.72	16.18	18.50
11	$ClCH_2Si(CH_3)_2OSi(CH_3)_2CH_2SCN$	35	Acetone	Na	38.4	105(1.5)	1.4691	1.0727	66.62	66.12	33.04 32.97	6.15 6.26	22.41 22.29	—	33.11	6.34	22.10	—
12	$(CH_3)_2SiCH_2CH_2CH_2SC_6H_7$		—	—	36.4	90(11)	1.4557	0.8518	60.71	61.28	—	—	—	—	—	—	—	—

TABLE 2

No.	Formula	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated [12]	Found in % C	Found in % H	Found in % Si	Found in % S	Calculated in % C	Calculated in % H	Calculated in % Si	Calculated in % S
1*	$(CH_3)_2SiCH_2SH$	71.5	116.9 (746)	1.4500	0.8516	37.05	38.07	—	—	—	—	—	—	—	—
2	$(C_6H_5)_2CH_2SiCH_2SH$	72.5	171.1 (735)	1.4658	0.8751	46.02	47.08	48.86 48.70	10.89 10.99	10.01 10.16	21.58 21.72	48.50	10.87	18.02	21.61
3	$(C_6H_5)_2CH_2SiCH_2SH$	68	43 (2)	1.4642	0.8689	56.03	56.59	55.47 55.52	11.34 11.37	15.30 15.13	16.05 16.69	54.47	11.43	15.91	18.17
4	$(C_6H_5)_2CH_2SiCH_2SH$	87	68 (1)	1.4640	0.8658	65.14	65.69	60.07 60.08	11.80 11.68	12.32 12.50	14.09 13.74	58.7	11.83	13.72	15.68
5	$(CH_3)_2SiCH_2CH_2CH_2SH$	30	164.2 (751)	1.4530	0.8491	47.29	47.33	—	—	—	—	—	—	—	—
6	$(CH_3)_2SiCH_2SCH_2CH_2CN$	88.5	250 (748)	1.4768	0.9420	51.06	51.90	48.55 48.42	8.77 8.67	16.16 16.28	18.06 18.79	48.50	8.72	16.18	18.49
7	$(C_6H_5)_2CH_2SiCH_2SCH_2CH_2CN$	79.5	100.5 (2)	1.4836	0.9443	60.06	60.02	53.68 53.63	9.44 9.47	13.81 13.63	15.87 16.14	53.67	9.51	13.93	15.92
8	$(C_6H_5)_2CH_2SiCH_2SCH_2CH_2CN$	70.5	124—125 (2)	1.4800	0.9301	70.07	70.42	57.93 57.80	10.01 9.97	12.25 12.05	13.30 13.22	57.58	10.10	12.23	13.97
9	$(C_4H_9)_2CH_2SiCH_2SCH_2CH_2CN$	72	147 (2)	1.4795	0.9172	79.67	79.42	60.98 60.73	10.47 10.58	10.67 10.57	12.23 12.40	60.63	10.57	10.89	12.45
10	$(CH_3)_2SiCH_2CH_2CH_2SCH_2CH_2CN$	71	108.5 (1)	1.4770	0.9287	61.26	61.16	53.64 53.87	9.56 9.63	13.83 13.87	16.02 16.15	53.62	9.51	13.93	15.92
11	$C_6H_5SCH_2Si(CH_3)_2CH_2SCH_2CH_2CN$	59	143 (2)	1.5110	1.0059	73.69	73.64	48.97 48.86	8.54 8.65	11.81 11.74	25.66 25.66	48.53	8.56	11.33	25.91

* The literature gives [6]: n_D^{20} 1.4502, d_4^{20} 0.8430, MR 38.50; [7]: n_D^{25} 1.4468, d_4^{25} 0.8329, MR 38.58.

thiol was obtained by the subsequent splitting of the isothiouronium salt with alkali.

By means of Reaction (5) we synthesized four organosilicon α-thiols, and two of these compounds [R_3 = $(CH_3)_3$ and $(C_2H_5)_2CH_3$] were distilled through an efficient column. On the basis of the constants of these compounds, we calculated the refraction of the mercaptomethyl group attached to silicon, the value found being 15.22 ml/mole. The α-thiols for which $R_3 = CH_3(C_2H_5)_2$ and $CH_3(C_4H_9)_2$ were vacuum distilled, but the products appeared to be contaminated with the corresponding sulfides, this view being confirmed by their elementary analyses and molecular refractions. Owing to the low yields of sulfides in Reaction (5), they were not isolated in the pure state.

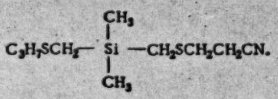
Reaction between an organosilicon γ-thiocyanate and n-C_3H_7MgBr, unlike the reaction of the α-thiocyanates, gave a considerable yield (37%) of the sulfide, and the γ-thiol was obtained in 40% yield:

$$2(CH_3)_2SiCH_2CH_2CH_2SCN + 2C_3H_7MgBr \longrightarrow$$
$$\longrightarrow (CH_3)_2SiCH_2CH_2CH_2SH + (CH_3)_2SiCH_2CH_2CH_2SC_3H_7. \quad (6)$$

Attempts to convert $(CH_3)_2Si(CH_2SCN)_2$ into $(CH_3)_2Si(CH_2SH)_2$ by the method described were unsuccessful. A substance was isolated, and its elementary analysis, and particularly the result of its cyanoethylation, indicated that the main products of the reaction were a mercapto sulfide and a disulfide:

$$2(CH_3)_2Si(CH_2SCN)_2 + 4C_3H_7MgBr \longrightarrow$$
$$\longrightarrow (CH_3)_2Si(CH_2SH)CH_2SC_3H_7 + (CH_3)_2Si(CH_2SC_3H_7)_2. \quad (7)$$

Cyanoethylation of the mixture of these substances gave a 59% yield of a compound which corresponded in elementary analysis and molecular refraction to



As we had a number of other organosilicon thiols at our disposal, we cyanoethylated them, so continuing our work [1,8] on the cyanoethylation of organosilicon compounds. In presence of sodium methoxide, both α- and γ-thiols add more vigorously to acrylonitrile than organosilicon alcohols [1] and amines [8] do:

$$R_3Si(CH_2)nSH + CH_2 = CHCN \longrightarrow R_3Si(CH_2)nSCH_2CH_2CN,$$

in which n = 1 and 3.

The properties of the compounds prepared in this investigation are given in Tables 1 and 2.

EXPERIMENTAL

Trimethyl(thiocyanatomethyl)silane $NCSCH_2Si(CH_3)_3$. A mixture of 97.3 g (1.2 moles) of sodium thiocyanate dissolved in 500 ml of 96% ethanol and 122.7 g (1 mole) of (chloromethyl)trimethylsilane [9] was prepared in a one-liter flask fitted with reflux condenser. The mixture was boiled for ten hours, the precipitated salt was filtered off, and alcohol was distilled from the filtrate. The liquid residue together with the previously separated salt were treated with water. The organic layer was separated and dried with calcium chloride. Vacuum distillation gave 122 g (84%) of trimethyl(thiocyanatomethyl)silane, b.p. 75° (10 mm). The remaining α-thiocyanates given in Table 1 were prepared under similar conditions.

Dimethylbisthiocyanatomethylsilane $(NCSCH_2)_2Si(CH_3)_2$. A mixture of 62.4 g (0.77 mole) of sodium thiocyanate, 400 ml of alcohol, and 55 g (0.35 mole) of bischloromethyldimethylsilane (formed in association with (dichloromethyl)trimethylsilane in the proportions of 1.8 : 1 in the chlorination of (chloromethyl)trimethylsilane [10]) was boiled for 11 hours. The usual treatment gave 55.9 g (79%) of dimethylbisthiocyanatomethylsilane, b.p. 142.5° (2 mm).

1,1,3,3-Tetramethyl-1,3-bisthiocyanatomethylsiloxane $O[(CH_3)_2SiCH_2SCN]_2$. A mixture of 15.8 g of sodium thiocyanate, 300 ml of acetone, and 22.2 g of 1,3-bischloromethyl-1,1,3,3-tetramethyldisiloxane [11] was boiled for 35 hours. The usual treatment gave 9.3 g (38.4%) of 1-(chloromethyl)-1,1,3,3-tetramethyl-3-(thiocyanatomethyl)siloxane, b.p. 104-105° (1 mm) and 14 g (52.5%) of 1,1,3,3-tetramethyl-1,3-bisthiocyanatomethylsiloxane, b.p. 148° (1 mm).

Trimethyl(3-thiocyanatopropyl)silane $NCSCH_2CH_2CH_2Si(CH_3)_3$. A mixture of 26 g (0.32 mole) of

sodium thiocyanate, 200 ml of alcohol, and 43.7 g (0.29 mole) of (3-chloropropyl)trimethylsilane (b.p.150.5° (744 mm); n_D^{20} 1.4319, and d_4^{20} 0.8789) was boiled for 16 hours. A yield of 36 g (71.5%) of trimethyl(3-thiocyanatopropyl)silane, b.p. 66.8° (1 mm), was obtained.

(Trimethylsilyl)methanethiol $HSCH_2Si(CH_3)_3$. Propylmagnesium bromide was prepared from 122 g (1 mole) of propyl bromide and 1 mole of magnesium in 500 ml of ether in a one-liter flask fitted with reflux condenser, dropping funnel, and stirrer. Trimethyl(1-thiocyanatomethyl)silane (47.3 g) was added dropwise to the Grignard reagent. Reaction was vigorous, and cooling was necessary. On the next day the contents of the flask were boiled for one hour and then decomposed with water and hydrochloric acid. The ether layer together with ether extracts from the aqueous layer was dried with sodium sulfate. Distillation through a column gave 28.1 g (71.5%) of (trimethylsilyl)methanethiol.

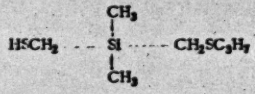
The organosilicon α-thiols listed in Table 2 were prepared similarly.

3-(Trimethylsilyl)-1-propanethiol $HSCH_2CH_2CH_2Si(CH_3)_3$. Trimethyl(3-thiocyanatopropyl)silane (34.7 g) was added to propylmagnesium bromide prepared from 15 g of magnesium and 95 g of propyl bromide in 250 ml of ether. The usual treatment gave 13.2 g (40%) of 3-(trimethylsilyl)-1-propanethiol, b.p. 164° and 13.9 g (36.6%) of $(CH_3)_3SiCH_2CH_2CH_2SC_3H_7$, b.p. 206°.

[Dimethyl(propylthiomethyl)silyl]methanethiol $HSCH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}CH_2SC_3H_7$. Dimethylbisthiocyanatomethylsilane (55 g) was added to propylmagnesium bromide prepared from 40 g of magnesium and 230 g of propyl bromide in 1 liter of ether. The usual treatment gave 42.3 g of a substance, b.p. 74.5° (2 mm); n_D^{20} 0.8674; d_4^{20} 0.8674.

Found %: C 46.38, 46.32; H 9.44, 9.48; S 28.66, 28.73; Si 13.54, 13.51. $C_4H_{12}SiS_2$. Calculated %: C 31.54; H 7.94; S 42.09; Si 18.43. $C_{10}H_{24}SiS_2$. Calculated %: C 43.24; H 9.33; S 32.98; Si 14.43. $C_7H_{18}SiS_2$. Calculated %: C 50.79; H 10.65; S 27.11; Si 11.87.

Cyanoethylation of product confirmed that it was



probably containing some $(C_3H_7SCH_2)_2Si(CH_3)_2$ as impurity.

3-[(Trimethylsilyl)methylthio] propionitrile $(CH_3)_3SiCH_2SCH_2CH_2CN$. One or two drops of sodium methoxide syrup were added to 12.2 g of (trimethylsilyl)methanethiol, and 10 g of acrylonitrile was then added at such a rate that the temperature did not rise above 50-60°. After one day the contents of the flask were washed with water acidulated with hydrochloric acid until they were neutral to litmus, and they were then dried with calcium chloride and distilled. The yield of 3-[(trimethylsilyl)methylthio]propionitrile was 14 g (88.5%); it boiled at 250° (748 mm). The other organosilicon thiols listed in Table 2 were cyanoethylated in a similar way.

SUMMARY

1. For the first time organosilicon compounds were prepared with a thiocyanato or thiol group in the γ-position with respect to silicon and also with two thiocyanato groups in α-positions.

2. It was shown that these organosilicon α- and γ-thiocyanates readily react with RMgX with formation of the corresponding thiols, which proves the structure of the thiocyanates and can form the basis of a new method of synthesizing organosilicon thiols.

3. It was found that organosilicon thiols, both the α and the γ compounds, readily add to acrylonitrile.

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REACTION OF HEXAALKYLDISILOXANES WITH IODINE AND ALUMINUM

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One of us recently proposed [1] a new method for the synthesis of trialkylhalosilanes based on the reaction of hexaalkyldisiloxanes with aluminum halides, which proceeds according to the equation:

$$R_3SiOSiR_3 + AlX_3 \longrightarrow 2R_3SiX + OAlX \quad (X = Cl, Br, \text{or } I).$$

This method, which is distinguished by its simplicity and by the high yields obtained, is somewhat inconvenient for the preparation of trialkyliodosilanes, since it demands the use of the unstable aluminum iodide, which is rarely found as a commercial product. For this reason we generally prepared aluminum iodide ourselves immediately before it was required for the reaction; for this purpose aluminum was treated with iodine in carbon disulfide or benzene. In order to obviate this procedure, we later attempted to replace aluminum iodide by a mixture of iodine and aluminum. It was found that trialkyliodosilanes are formed smoothly when a mixture of the hexaalkyldisiloxane, aluminum, and iodine, taken in the molecular proportions 1 : 1.1 : 1.5, is heated until the color of the iodine disappears. Fractional distillation of the reaction mixture gives trialkyliodosilanes in 82-93% yield. In this way we prepared five trialkyliodosilanes (the tributyl and triisopentyl compounds had not been prepared previously). Their physical properties and yields and the analytical data are given in the table.

TABLE

Trialkyliodosilanes R_3SiI

R	B.p. in °C ± 0.5° (p in mm)	d_4^{20} ±0.001	Yield (%)	Found I (%)	Calculated I (%)
CH_3	107.5 (760)	1.422	93	63.8; 64.1	63.42
C_2H_5	191.2 (760)	1.351	89	52.7; 52.5	52.39
$n\text{-}C_3H_7$	238 (760)	1.229	88	44.4; 44.7	44.65
$n\text{-}C_4H_9$*	124.5—125.5 (4)	1.225	85	39.1; 38.5	38.89
$i\text{-}C_5H_{11}$*	151—152 (5)	1.115	82	34.5; 34.0	34.45

* New compound

EXPERIMENTAL

Original hexaalkyldisiloxanes. These were prepared and purified as described previously [2]. Hexaisopentyldisiloxane, which has not been described previously had b.p. 210-211° (8 mm); d_4^{20} 0.8398; n_D^{20} 1.4467; $n_F^{20} - n_C^{20}$ 0.0083; Si 11.49 and 11.30%; calculated Si 11.26%. The other reactants were aluminum fillings, containing 99.6% Al, and chemically pure iodine powder.

Determination of iodine in trialkyliodosilanes. A sample of the substance (0.15-0.3 g) contained in a sealed tube was introduced into a measured amount (20-30 ml) of 0.1 N NaOH contained in a flask having a ground-in stopper. The tube was broken, the contents of the flask were carefully mixed, and the solution was allowed to stand for 15 minutes at room temperature. Excess of alkali was then titrated to phenolphthalein with 0.1 N HCl.

Procedure in the syntheses. The hexaalkyldisiloxane, aluminum, and iodine, taken in the molecular proportions of 1 : 1.1 : 1.5, were introduced into a flask fitted with a 20-cm Vigreux column. The reaction mixture was gradually heated to the boil and maintained at that temperature until the iodine color disappeared (30-60 minutes); it was then distilled under diffuse illumination in a nitrogen atmosphere (in a vacuum in the case of triisopentyliodosilane)•. Reaction was sometimes vigorous, and the distillation flask was cooled with water. The trialkyliodosilanes then obtained were immediately redistilled over copper powder under diffuse illumination in an atmosphere of pure dry nitrogen. High-boiling trialkyliodosilanes were immediately redistilled under a reduced pressure of nitrogen. The trialkyliodosilanes, purified in this way, were quickly sealed in glass tubes filled with nitrogen and were kept in the dark. Analyses and determinations of physical constants were carried out on the trialkyliodosilanes as soon as possible after their preparation. All operations with trialkyliodosilanes were carried out with the appropriate precautions against the introduction of traces of moisture. By way of examples, some of the syntheses are described below.

Synthesis of iodotrimethylsilane. Aluminum filings (5.4 g, i.e. 0.2 g-atom) and iodine powder (67.1 g, i.e. 0.558 g-atom) were added to hexamethyldisiloxane (30.5 g, i.e. 0.186 mole). The mixture was heated at the boil until the iodine color disappeared (1 hour), and it was then distilled under diffuse illumination in an atmosphere of nitrogen. The yield of iodotrimethylsilane, b.p. 105.5-107° (752 mm), was 54.5 g (93%).

Synthesis of tributyliodosilane. A mixture of 62.2 g (0.15 mole) of hexabutyldisiloxane, 4.9 g (0.18 g-atom) of aluminum filings and 57.15 g (0.45 g-atom) of iodine was heated at the boil until the iodine color disappeared (1 hour). Distillation of the reaction mixture under diffuse illumination in an atmosphere of nitrogen gave 83.4 g (85%) of tributyliodosilane, b.p. 280-282.5° (755 mm).

Synthesis of odotriisopentylsilane. A mixture of 25.5 g (0.05 mole) of hexaisopentyldisiloxane, 2.66 g (0.09 g-atom) of aluminum filings, and 19.1 g (0.15 g-atom) of iodine was heated at the boil until the iodine color disappeared (1 hour). Vacuum distillation gave 30.1 g (82%) of iodotriisopentylsilane, b.p. 136-145° (4 mm).

SUMMARY

A method was developed for the synthesis of trialkyliodosilanes by reaction between hexaalkyldisiloxanes, iodine, and aluminum.

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•. Vacuum distillation of the reaction mixture, which we carried out for the syntheses of tripropyl- and tributyl-iodosilanes, did not result in higher yields.

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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 10. STEREOCHEMISTRY OF THE DIENE CONDENSATION OF 1-VINYL-1-CYCLOHEXENE WITH MALEIC ANHYDRIDE

I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

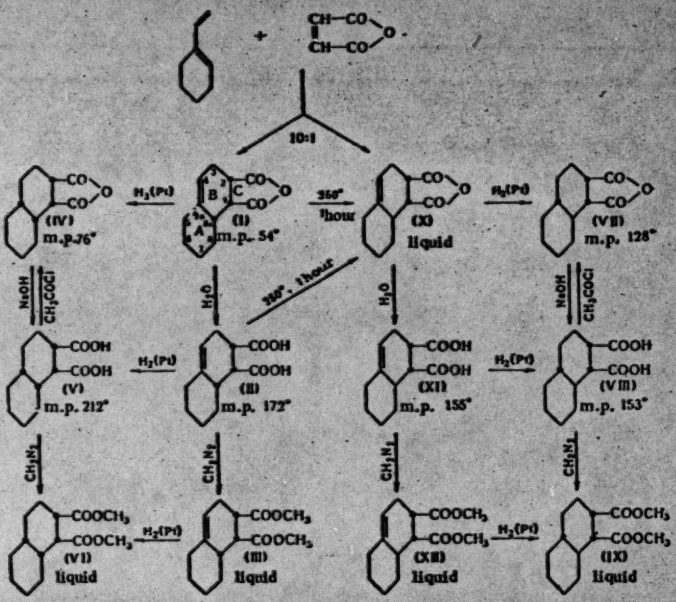
Our previous investigations on the condensation of 1-vinyl-1-cyclohexene [1] and 1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinylnaphthalene [2] with citraconic anhydride enabled us to establish some interesting stereochemical peculiarities of these diene syntheses. These peculiarities, in particular the configurations of the isomers formed and the steric selectivity of the hydrogenation reaction, were established in the greatest detail for the condensation of 1-vinyl-1-cyclohexene with methyl acrylate [3]. In order to carry our study of the stereochemistry of the diene synthesis still further, we investigated the condensation of 1-vinyl-1-cyclohexene with maleic anhydride [4]. It was found that this reaction proceeds extremely readily: simple mixing of the components at room temperature results in a vigorous exothermic reaction with formation of a mixture of adducts, from which only a small amount (10-15%) of the previously described [5] crystalline cis anhydride (I), m.p. 53-54°, could be isolated. When the reaction was carried out under milder conditions (stirring a benzene solution at 2-3° for 120 hours), a 55% yield of the cis anhydride (I) was obtained together with about 15% of a liquid product of the diene synthesis.

In accordance with the results obtained for 1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid [3], the cis anhydride (I) formed under such mild conditions will have cis configurations of the hydrogen atoms at C-1, C-2, and C-8a [6] and, in accordance with the nomenclature adopted for tetradecahydrophenanthrenes [7], should be referred to as a syn-cis anhydride. When boiled with water, it is readily hydrolyzed with formation of the corresponding syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid (II), which is converted by diazomethane into the syn-cis diester (III).

As in all other analogous cases that we have studied [1-3], the hydrogenation over a platinum catalyst of the compounds (I), (II), and (III) proceeds sterically in a strictly selective fashion with formation of only one of the possible isomers. Owing to the screening effect of the ortho carboxyls, which we proved for the cases of 1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acid [3] and 4-methyl-4-cyclohexene-1,2-dicarboxylic acid [8], the addition of hydrogen to (I), (II), and (III) proceeds exclusively from the side opposite to the carboxyls, resulting in the formation of the saturated anhydride (IV), m.p. 76°, the acid (V), m.p. 212°, and the diester (VI), which have the cis-syn-cis configuration and belong to the cis-decahydronaphthalene series.

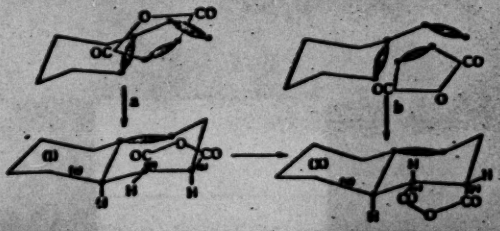
The liquid product of the diene synthesis, which did not crystallize after long standing and treatment with solvents, was readily hydrogenated over a platinum catalyst at room temperature with the absorption of one molecular equivalent of hydrogen, and a 30% yield was obtained of the individual saturated cis anhydride (VII), m.p. 128°, which differed from the cis-syn-cis anhydride (IV) and gave a new cis acid (VIII), m.p. 153°, when hydrolyzed. This fact, which definitely pointed to the presence of the isomeric anti-cis anhydride (X) in the liquid mixture of adducts, prompted us to study the thermal isomerization of the syn-cis anhydride (I) and the syn-cis acid (III), for it is known [8,9] that the thermal isomerization of syn-cis ortho-dicarboxylic acids readily results in their conversion into more stable isomers having the anti-cis configuration.

It was, in fact, found that the anhydride (I) and the acid (II), heated for one hour at 250° and then vacuum distilled, are isomerized in good yield to the liquid anti-cis anhydride (X), which is hydrolyzed by water to the anti-cis acid (XI), which can be converted by diazomethane into the anti-cis diester (XIII).



Like the Compounds (I), (II), and (III) of the syn-cis series, the anti-cis Compounds (X), (XI), and (XII) are also readily and sterically selectively hydrogenated over a platinum catalyst with formation of only one isomer in each case. Such selective hydrogenation, as in all the other analogous cases that we have studied, is due to the screening effect of carboxyl groups, as a result of which addition of hydrogen proceeds only from the side opposite to the carboxyls, with formation of the saturated anhydride (VII), acid (VIII), and diester (IX), which have a trans-anti-cis configuration and belong to the trans-decahydronaphthalene series. It was thus shown that, even under mild conditions, the condensation of 1-vinyl-1-cyclohexene with maleic anhydride results in the simultaneous formation of syn-cis and anti-cis anhydrides, (I) and (X), in the ratio of about 10 : 1.

The thermal isomerization of the syn-cis anhydride (I) into the anti-cis anhydride (X), and also the readiness with which the Compounds (X), (XI), and (XII) of the anti-cis series are hydrogenated, shows that the latter differ from the corresponding compounds of the syn-cis series, (I), (II), and (III), only in the disposition of the hydrogen at C-8a. An examination of molecular models fully confirms this inference and at the same time explains the steric selectivity of hydrogenation.



It follows from the general scheme of the diene synthesis that the addition of maleic anhydride to 1-vinyl-1-cyclohexene can proceed in two possible directions (a and b), of which a is predominant under mild conditions and gives an adduct of the syn-cis configuration (I). Condensation in the direction b, being energetically less favorable, goes with greater difficulty and gives a stable anhydride of the anti-cis configuration (X), which is epimeric to (I) with respect to the hydrogen at C-8a.

The anti-cis anhydride (X) has the energetically most favorable (e)-(e) disposition * of ortho-substituents and (e)-(p) disposition of meta-substituents, so that the anhydride (X) and other compounds of this series are thermally more stable than the syn-cis anhydride (I). The models show that the carboxyls have a screening effect in the isomeric anhydrides (I) and (X), and this results in sterically selective hydrogenation such that in the syn-cis anhydride (I) it must result in a cis-decahydronaphthalene system, and in the anti-cis anhydride (X) it must result in a trans-decahydronaphthalene system.

By further detailed investigations of the chemical transformations of these compounds, we completely confirmed these conclusions and rigorous proof was obtained of the spatial configurations - as epimers with respect to hydrogen at C-8a – of the syn-cis and anti-cis anhydrides (I) and (X).

EXPERIMENTAL **

Condensation of 1-Vinyl-1-cyclohexene with Maleic Anhydride

A solution of 98.5 g of freshly distilled maleic anhydride in 375 ml of absolute cryoscopic benzene containing a little pyrogallol (0.2-0.5 g) was placed in a three-necked flask fitted with mechanical stirrer, dropping funnel, thermometer, and calcium chloride tube. The flask was cooled to 2-3°, and the contents were stirred while 108 grams (1 mole) of 1-vinyl-1-cyclohexene (distilled over sodium; b.p. 142-144°; n_D^{20} 1.4960) was added over a period of 90 minutes. Stirring at this temperature was continued for 120 hours, and the benzene was then distilled off under reduced pressure (bath temperature not above 35°). The oily residue was left for two days at room temperature and was then cooled with ice for 2-3 hours. Oil was pressed from the crystals on the filter, and the crystals were then washed twice with 50-ml portions of a 1 : 3 mixture of diethyl ether and petroleum ether and then once with 50 ml of a 1 : 1 mixture of diethyl ether and petroleum ether. The product was 81.5 g of the syn-cis anhydride (I), m.p. 51-53°. The substance was purified by dissolving it in 100 ml of absolute ether, filtering off the polymer that separated, and diluting the solution with 150 ml of petroleum ether, when 66.5 g of pure syn-cis anhydride (I), m.p. 53-54°, was obtained [4]. Evaporation of the mother liquor to dryness and crystallization of the residue gave a further 8 g of pure anhydride (I). In all, therefore, 74.5 g (38%) of the anhydride was obtained.

The mother liquors were evaporated under reduced pressure, and the residual liquid was left at 0° for two days. The crystals that separated were pressed on the filter to remove oil and washed with a 1 : 2 mixture of diethyl ether and petroleum ether. The product was 36.7 g of a crystalline substance, m.p. 29-37°. Further evaporation of the mother liquor and cooling with ice and salt gave another 5.6 g of crystals, m.p. 33-42°. No more crystals were obtained when the residue was again cooled.

The low-melting crystalline product so obtained could not be purified from maleic anhydride, and it was hydrolyzed at the boil with water for 15 minutes. The polymer that separated from the solution was filtered off, 5 ml of acetone was added, and the mixture was left overnight. The substance that separated, amounting to 21 g, was the syn-cis-acid (II), m.p. 170-171°, and after crystallization from 20% aqueous acetone it had a constant melting point of 171-172° [4].

Found %: C 64.03, 64.05; H 7.18, 7.09. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.
Found %: M 221.7 (titration with NaOH). Calculated %: M 224.3.

The diphenacyl ester, prepared in the usual way, melted at 142-143° (from 80% alcohol), which corresponds to data in the literature [5].

The aqueous mother solution obtained after the separation of the syn-cis acid (II) was evaporated to dryness, and washing of the crystalline residue with benzene and then with ether yielded 7.3 g of maleic acid, m.p. 132-134°, undepressed by admixture of a known sample (131-133°). The total yield of the syn-cis adduct (I) calculated on the anhydride (I) was 53%.

* The symbol (e) denotes an equatorial disposition of a substituent, and the symbol (p) a polar disposition.
** All melting points are corrected.

The liquid product of the diene synthesis was twice distilled under reduced pressure and gave 29.5 g of a light-yellow viscous liquid, b.p. 169-170° (3 mm) and n_D^{20} 1.5214. This substance was dissolved in 60 ml of cryoscopic benzene and hydrogenated over platinum oxide, when 4670 ml (about 1.5 molecular equivalents) of hydrogen was absorbed. Solvent was distilled off, and the liquid residue was allowed to stand, when it partially crystallized. Washing of the hydrogenation product on the filter with a 1 : 2 mixture of benzene and petroleum ether gave 10.4 g of the trans-anti-cis anhydride (VII), m.p. 121-123°, which melted constantly at 127-128° after crystallization from a 1 : 1 mixture of benzene and petroleum ether (glistening scales).

Found %: C 69.34, 69.19; H 7.71, 7.59. $C_{12}H_{14}O_3$. Calculated %: C 69.21; H 7.74.

syn-cis Dicarboxylic Acid (II)

A mixture of 1.0 g of the syn-cis anhydride (I) and 5 ml of water was boiled for 15 minutes. Acetone (1 ml) was added to the warm solution, and when cold, the solution yielded 0.95 g of the syn-cis dicarboxylic acid (II), which after crystallization from 20% aqueous acetone melted at 171-172° and showed no melting point depression in admixture with the acid obtained previously (above).

In order to reconvert it into the syn-cis anhydride (I), the syn-cis acid (II) (0.35 g) was boiled for 15 minutes with 3.5 ml of acetic anhydride, which was then distilled off under reduced pressure. Crystallization of the residue from a mixture of diethyl ether and petroleum ether gave 0.15 g of the anhydride (I), m.p. 51-52°, which was found to be identical with the product described above. When the syn-cis acid (II) was boiled with acetyl chloride, an oily chlorine-containing product was obtained.

syn-cis Diester (III)

A suspension of 8.5 g of the syn-cis acid (II) in ether was treated with excess of ethereal diazomethane. Ether was distilled off, and vacuum distillation of the residue gave 8.7 g of syn-cis diester (III), b.p. 126-127° (2 mm); n_D^{20} 1.5000; d_4^{20} 1.1419; found MR 65.0; calculated MR 65.29.

Found %: C 66.70, 66.74; H 8.08, 7.98. $C_{14}H_{20}O_4$. Calculated %: C 66.65; H 7.99.

cis-syn-cis Anhydride (IV)

The syn-cis anhydride (I) (10 g) was dissolved in cryoscopic benzene (100 ml) and hydrogenated over 0.1 g of platinum oxide. One molecular equivalent of hydrogen (1100 ml at 0° and 760 mm) was absorbed. Solvent was distilled off under reduced pressure, and the liquid residue rapidly crystallized when treated with petroleum ether. Recrystallization from 100 ml of a 1 : 2 mixture of diethyl ether and petroleum ether gave 8.2 g of the cis-syn-cis anhydride (IV), m.p. 72-74°. A further 1.3 g of the same saturated anhydride, m.p. 72-74°, was isolated after two crystallizations from the mother liquor. After further recrystallization the substance melted at 75-76°.

Found %: C 69.42, 69.24; H 7.83, 7.89. $C_{12}H_{14}O_3$. Calculated %: C 69.21; H 7.74.
The other possible isomer was not isolated.

cis-syn-cis Dicarboxylic Acid (V)

a) A mixture of 4.2 g of the cis-syn-cis anhydride (IV) and 35 ml of 5% aqueous caustic soda was boiled for 15 minutes, filtered, and acidified with hydrochloric acid. A substance (4.3 g) of m.p. 200-203° was obtained. Crystallization from 80% aqueous acetone gave pure cis-syn-cis dicarboxylic acid (V), melting constantly at 211-212°. When (V) was heated with acetyl chloride, (IV) was obtained in high yield.

Found %: C 63.58, 63.72; H 7.98, 7.86. $C_{12}H_{16}O_4$. Calculated %: C 63.68; H 8.02.

b) The syn-cis acid (II) (12.0 g) was dissolved in absolute methanol and hydrogenated in presence of 0.2 g platinum oxide. Hydrogenation was very rapid, and in one hour one molecular equivalent of hydrogen (1200 ml) was absorbed. Catalyst was filtered off, methanol was distilled off under reduced pressure, and the crystalline residue was washed on the filter with 50% acetone. An almost quantitative yield (11.3 g) was obtained of the cis-syn-cis dicarboxylic acid (V), m.p. 207-210°. After crystallization from 80% acetone it melted at 211-212°, and there was no depression in a mixture melting point test with the sample obtained in the preceding experiment. No other crystalline substance could be isolated from the mother liquor.

cis-syn-cis Diester (VI)

a) A suspension of 5 g of the cis-syn-cis dicarboxylic acid (V) in ether was treated with excess of ethereal diazomethane. Ether was distilled off, and vacuum distillation of the residue gave 5.1 g of the cis-syn-cis diester (VI), b.p. 130-131° (2 mm), n_D^{20} 1.4902; d_4^{20} 1.1229; found MR 65.76, calculated MR 65.48.

Found %: C 66.0, 65.96; H 8.85, 8.68. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

b) The syn-cis diester (III) (5.5 g) was dissolved in methanol and hydrogenated over platinum oxide. One molecular equivalent of hydrogen (490 ml) was absorbed. Methanol was distilled off, and vacuum distillation of the residue gave 5.3 g of the above-described cis-syn-cis diester (VI), b.p. 130-131° (2 mm) and n_D^{20} 1.4908.

anti-cis Anhydride (X)

a) The syn-cis anhydride (I) (5.0 g) was heated at 245-255° in a current of nitrogen for 45 minutes, and the reaction product was vacuum distilled (25 mm) at a bath temperature of 220-230°. Redistillation gave 3.3 g (66%) of pure anti-cis anhydride (X) in the form of a thick yellowish oil, b.p. 177-178° (8 mm) and n_D^{20} 1.5224.

Found %: C 69.60, 69.70; H 8.83, 8.82. $C_{12}H_{16}O_3$. Calculated %: C 69.88; H 6.84.

b) The syn-cis acid (II) (9.0 g) was heated in a current of nitrogen at 245-250° for 50 minutes. Vacuum distillation gave 6.7 g of the above-described anti-cis anhydride (X), b.p. 185-187° (11 mm) and n_D^{25} 1.5230.

Hydrogenation of the anti-cis Anhydride (X)

The anti-cis anhydride (X) (2.0 g) was dissolved in cryoscopic benzene (20 ml) and hydrogenated over a platinum catalyst. One molecular equivalent of hydrogen (220 ml) was absorbed. Benzene was distilled off, and the treatment of the residue with petroleum ether gave 1.75 g of the trans-anti-cis anhydride (VII), m.p. 123-124°. Crystallization from ether gave an anhydride of constant melting point (126-127°), which was found to be identical with the substance isolated directly from the liquid product of the diene synthesis.

anti-cis Dicarboxylic Acid (XI)

A mixture of 20.3 g of the liquid anti-cis anhydride (X) and 100 ml of water was boiled until complete solution occurred and was then boiled further for 15 minutes. As the solution cooled, acetone was added (about 20 ml in all) so that the oil that tended to separate was maintained in solution. The mixture was set aside at room temperature for three days. The crystals that separated were filtered off. The product was 11.5 g of (XI); after being vacuum dried at 80° and crystallized from 10% aqueous acetone, it had constant m.p. 154-155°. Evaporation of the mother liquor gave a further 1.5 g of (XI). Found %: C 64.53, 64.43; H 7.29, 7.34. $C_{12}H_{18}O_4$. Calculated %: C 64.27; H 7.19. The dibenacyl ester melted after crystallization from ethanol at 119-120°. Found %: C 73.23, 73.01; H 6.14, 6.09. $C_{32}H_{34}O_6$. Calculated %: C 73.02; H 6.13.

anti-cis Diester (XII)

A suspension of 3.75 g of the anti-cis acid (XI) in ether was treated with ethereal diazomethane. Solvent was distilled off, and vacuum distillation of the residue gave 3.8 g of the anti-cis diester (XII), b.p. 133-134° (3 mm), n_D^{20} 1.4970, d_4^{20} 1.1233; found MR 65.14; calculated MR 65.29.

Found %: C 66.65, 66.63; H 8.06; 7.89. $C_{14}H_{22}O_4$. Calculated %: C 66.65; H 7.99.

trans-anti-cis Dicarboxylic Acid (VIII)

a) A mixture of 8.0 g of the trans-anti-cis anhydride (VII) and 50 ml of 5% aqueous caustic soda was boiled for ten minutes. The solution was filtered and acidified with hydrochloric acid. The oil that separated rapidly solidified. The product was 8.3 g of the trans-anti-cis dicarboxylic acid, m.p. 152-153°. Recrystallization from a mixture of water with a little acetone did not affect the melting point.

Found %: C 63.64, 63.54; H 7.96, 7.76. $C_{12}H_{18}O_4$. Calculated %: C 63.68; H 8.02.

The acid (VIII) so obtained showed a large depression in melting point in admixture with the anti-cis dicarboxylic acid (XI). Boiling of the trans-anti-cis acid (VIII) with acetyl chloride resulted in a quantitative yield of the original trans-anti-cis anhydride (VII).

b) The anti-cis dicarboxylic acid (XI) (5.0 g) was dissolved in 100 ml of absolute methanol and hydrogenated in presence of 0.1 g of platinum oxide. Hydrogenation was rapid, and one molecular equivalent of hydrogen (510 ml) was absorbed. Methanol was distilled off, and the oily residue crystallized when a little water was added. The product was 4.2 g of the trans-anti-cis dicarboxylic acid (VIII), m.p. 149-151°. After being crystallized from 20% aqueous acetone, the acid had m.p. 151-152°, undepressed by admixture of the sample obtained in the preceding experiment. No other crystalline product could be isolated from the mother liquors.

trans-anti-cis Diester (IX)

a) A suspension of 6.3 g of the trans-anti-cis dicarboxylic acid (VIII) in ether was treated with ethereal diazomethane. Distillation gave 5.6 g of the trans-anti-cis diester (IX), b.p. 122-123° (2 mm), n_D^{20} 1.4809, d_4^{20} 1.1051; found MR 65.47, calculated MR 65.48.

Found %: C 65.81, 65.82; H 8.67, 8.74. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

b) The anti-cis diester (XI) (6.1 g) was dissolved in absolute methanol (40 ml) and hydrogenated over platinum oxide. One molecular proportion of hydrogen was absorbed. The catalyst was filtered off, methanol was distilled off, and the residue was vacuum distilled, when 5.5 g of the above described trans-anti-cis diester (IX), b.p. 121-122° (2 mm) and n_D^{20} 1.4810.

SUMMARY

1. A study was made of the diene condensation of 1-vinyl-1-cyclohexene with maleic anhydride. It gives the syn-cis and anti-cis anhydrides (I) and (X) in the proportions of 10 : 1. These isomers differ in the disposition of the hydrogen at C-8a.

2. The thermal transformation of the syn-cis anhydride (I) into the anti-cis anhydride (X) was effected, and the corresponding isomeric acids (II) and (XI) and isomeric esters (III) and (XII) were prepared.

3. It was shown that the hydrogenation of derivatives both of the syn-cis series (I, II, III) and also of the anti-cis series (X, XI, XII) proceeds in a sterically selective manner: hydrogen adds from the least screened side (opposite to the carboxyl groups) with formation of derivatives of the cis- and trans-decahydronaphthalene series respectively.

4. An examination of molecular models has enabled us to explain the spatial configurations of the adducts obtained, (I) and (X), and also the steric selectivity of the hydrogenation of these and other compounds obtained.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 16. HYDROCONDENSATION OF CARBON MONOXIDE WITH 1-BUTENE

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In a previous investigation [1] it was shown that liquid hydrocarbons are obtained in yields of up to 540 ml/cu.m or 55.5 ml/liter·hour in the hydrocondensation of carbon monoxide with 2-butene at 190° under atmospheric pressure, the composition of the original gas mixture being 4-6% of carbon monoxide, 70-75% of 2-butene, and 21-26% of hydrogen. 2-Butene reacts to the extent of 47%, of which 5% is hydrogenated to butane. The liquid condensate, when freed from C_4 hydrocarbons, contains 37% of unsaturated hydrocarbons, and after being hydrogenated, 76% of it boils within the range 36-332°. The reaction product is composed mainly of normal aliphatic hydrocarbons in admixture with a small amount of only slightly ramified branched hydrocarbons, where there is probably only one methyl side group, this being on the second carbon atom of the chain. The results indicate that, in the hydrocondensation of carbon monoxide with 2-butene, most of the latter isomerizes into 1-butene, which then reacts with carbon monoxide and hydrogen with predominant formation of hydrocarbons of normal structure.

In view of these results it was of interest to investigate the hydrocondensation of carbon monoxide with 1-butene under similar conditions. We have previously reported [2] the results of an investigation of the hydrocondensation of carbon monoxide with the n-butene obtained by dehydration of 1-butanol over alumina; this consisted predominantly of 1-butene, but the relative amounts of the isomers were not determined exactly. In these experiments we used an equimolecular mixture of butene and hydrogen containing 4-6% of carbon monoxide. Yields of liquid hydrocarbons of up to 635 ml/cu.m or 55 ml/liter·hour were obtained. The debutanized liquid condensate boiled over the range 28-276°, contained 28% of olefins, and, when hydrogenated, was found to contain about 24% by volume of C_5 hydrocarbons (about one-half of it isopentane), 15% of C_6, 8% each of C_7 and C_8, and 9% of C_9. About 30-35% of the butene was hydrogenated to butane. As will be seen from the data cited, the butene:hydrogen ratios differed greatly in investigations [1] and [2]: in the first it was 1 : 1, and in the second 2.7-3 : 1. In an investigation of the effect of the concentration of carbon monoxide on the course of the hydrocondensation of carbon monoxide with butene [3], it was shown that reaction was most rapid when the carbon monoxide content of the original gas was 6-8%. At 15-20% CO the yield of heavy hydrocarbons increased rapidly and the process, unlike the similar process with ethylene, was greatly retarded. It is possible that this explains the results obtained in a study of the behavior of 1-butene and cis-2-butene [4] under the conditions of gasoline synthesis over a Co-Cu-ThO_2 catalyst at 190° when added to the extent of 1.6-2.3% to an original gas mixture of 1 CO : 1.7 H_2. It was found that only a small proportion of the butene was converted into high-boiling oxygen compounds. Most of it was found in the C_4 fraction of the synthesis products, and it had no effect on the yield and composition of the C_5 fraction. In these experiments [4], 58.5% of the added 2-butene remained unchanged, 29.1% was hydrogenated to butane, and 3.6% was isomerized to 1-butene; 6.4% of the added 1-butene remained unchanged, 40.0% was converted into butane, and 28.2% was isomerized to 2-butene.

The object of the present work was the investigation of the hydrocondensation of carbon monoxide with 1-butene and the effect of additions of 10-30% of 2-butene on the course of the reaction. It was shown previously [5] that, in presence of hydrogen but in absence of carbon monoxide, 1-butene is isomerized to 2-butene in presence of a hydrocondensation catalyst at 190°; the relative amounts of 1- and 2-butenes in the products was 1 : 1.1. It would be expected that, under the same conditions but in presence of carbon monoxide, 1-butene would be converted to a certain extent into 2-butene, and additions of the latter in amounts of 10-35% would have no effect on the course of the hydrocondensation of 1-butene with carbon monoxide.

EXPERIMENTAL

Preparation of 1-Butene and of Its Mixtures with 2-Butene

1-Butene and its mixtures with various amounts of 2-butene were prepared by the dehydration of 1-butanol [b.p. 116.5 - 117.0° (756 mm); n_D^{20} 1.3991; d_4^{20} 0.8098; found MR 22.13; calculated C_4H_9OH MR 22.20] under various conditions over alumina prepared in various ways, differing according to the proportion of admixed 2-butene required. The method of determining the composition of the C_4 fraction was described previously [5].

It must be pointed out that there are some extremely contradictory statements in the literature about the compositions of n-butene mixtures obtained by the dehydration of 1-butanol over alumina. This is to be attributed to imperfect methods of analysis [5] and to a lack of appreciation of the effect of differences in the composition and properties of the alumina preparations used [6,7].

The activity of the catalyst with respect to the displacement of the double bond is to be attributed not to the aluminum hydroxide itself, but to acidic impurities [8], and therefore, depending on the method of preparing the catalyst – in particular, on the temperature at which it is calcined before use ("acidic" impurities are decomposed during calcination) – and also on the reaction temperature and time of contact with the catalyst, the 2-butene content of the gas obtained may vary over a wide range and may attain 90%. Table 1 gives the compositions of the original gas mixtures used in the present investigation.

TABLE 1

Catalyst No.	Experiment No.	Duration of experiment (hours)	Space velocity ($hour^{-1}$)	Contraction (%)	Composition of original gas (% by volume)				Yield (ml/cu.m)			Yield of (H+L) (ml/liter-hour)
					1-Butene	2-Butene	H_2	CO	Heavy Oil (H)	Light Oil (L)	H + L	
77	306	4.8	101	50.7	72.7	0.0	22.7	4.6	410.9	410.9	821.8	83.0
77	307	7.5	102	44.2	64.8	7.2	23.6	4.4	349.9	393.0	742.3	75.5
77	308	7.0	102	41.6	64.4	7.2	23.7	4.7	429.9	350.4	780.3	79.5
77	309	7.0	98	39.0	67.7	6.7	19.6	6.0	365.8	365.8	731.6	71.4
77	310	7.0	100	51.0	62.4	10.6	22.6	4.4	404.8	571.4	976.2	97.6
77	311	23.5	104	46.0	61.9	10.5	22.1	5.5	243.5	526.0	769.5	80.5
78	312	19.0	101	48.4	64.4	10.9	20.6	4.1	384.3	522.1	906.4	92.3
79	313	21.5	103	44.3	60.9	10.3	23.5	5.3	177.0	685.6	862.6	89.3
80	314	13.0	100	47.0	45.8	24.7	24.5	5.0	475.0	500.0	975.0	100.0

For the preparation of the mixture used in Experiment 306, pure 1-butene was obtained by the method described previously [5]; it did not contain 2-butene or isobutene, and its vapor pressure at 0° (p_0) was 963 mm, which corresponds to 100% 1-butene. For Experiments 307, 308, and 309 we used a mixture of 90-91% of 1-butene and 9-10% of 2-butene (p_0 941-945 mm) obtained by the dehydration of 1-butanol over commercial alumina at 360-370° in a porcelain tube of internal diameter 20 mm, the space velocity of the 1-butanol being 6.7 $hour^{-1}$. For Experiments 310-313 we prepared a mixture of 85.5% of 1-butene and 14.5% of 2-butene (p_0 930 mm) by dehydration in the same tube at 400° at a space velocity of the alcohol of 4.1 $hour^{-1}$ over alumina prepared as follows: precipitation with caustic soda from aluminum nitrate solution, conversion into sodium aluminate, reprecipitation from this with ammonium chloride [9]. Before use in the reaction the catalyst was calcined in a stream of air at 450° for four hours. The butene mixture of highest 2-butene content was used for the preparation of the original gas mixture for Experiment 314; it contained 70% of 1-butene and 30% of 2-butene (p_0 893 mm), and was obtained by the dehydration of 1-butanol over commercial alumina at 400° in a porcelain tube of internal diameter 14 mm, the space velocity of the 1-butanol being 4.1 $hour^{-1}$.

Hydrocondensation of Carbon Monoxide with 1-Butene and with Its Mixtures with 2-Butene

Table 1 gives the results of experiments on the catalytic hydrocondensation of carbon monoxide with 1-butene and with butene mixtures containing 65-90% of 1-butene and 35-10% of 2-butene. These experiments were carried out in a flow system at 190° and atmospheric pressure. The apparatus and procedure were the same as those used previously [1]. The reactor was a glass tube, 12 mm in diameter. The catalysts used

ns, 77-80) were all of the same composition and were prepared in the same way. They were used in 30-ml portions and were regenerated after they had been in use for 15-20 hours. The original gas mixtures contained 46-53% of 1-butene, 0.0-25% of 2-butene, 20-24.5% of hydrogen, and 4-6% of carbon monoxide, and they were passed over the catalyst at a space velocity of about 100 hour $^{-1}$. As will be seen from Table 1, the yield of liquid hydrocarbons (calculated on $C_4H_8 + H_2 + CO$) was 730-975 ml/cu.m, or 70-100 ml per liter of catalyst per hour, the contraction in the original gas being 40-50%. The ratio of heavy oil to light was about unity after the catalyst had been in work for about ten hours, and it was 0.25-0.73 after about 20 hours.

These results show that, as was to be expected, addition of 2-butene to the original mixture and gradual increase in its content within the range indicated do not bring about any regular changes in the course of the hydrocondensation reaction between carbon monoxide and 1-butene. The somewhat higher yield of hydrocarbons, as expressed in ml/cu.m or ml/liter·hour, in Experiments 310-314 is associated with a relative increase in the yield of the light oil (mainly owing to the longer working period of the catalyst) with a consequent increase in the volume of condensate. In one series of experiments, the composition of the outgoing gas was investigated in detail and, on the basis of the data obtained on the composition of the original gas and its contraction, the extent to which components of the original gas mixture took part in the process was determined. By way of example, we will give the relevant data for Experiment 306, in which the hydrocondensation of carbon monoxide with 100% 1-butene was carried out. In this experiment we took 14.6 liters (STP) of a gas mixture of composition 72.7% of 1-butene, 22.7% of hydrogen, and 4.6% of carbon monoxide, and apart from liquid condensate we obtained 7.2 liters of gas, of which 2.9 liters was fractionally distilled, for the purpose of analysis, through a Podbielniak low-temperature column. The results of the fractionation are shown in Table 2 and Fig. 1; Fractions III and IV did not contain isobutene.

It was shown, on the basis of the data given in Tables 1 and 2, that hydrogen reacted to the extent of 55.3%, carbon monoxide to the extent of 52.2%, and 1-butene to the extent of 76.2%: 7.2% of the original 1-butene (9.4% of that which reacted) was hydrogenated to butane, 9.4% (12.4% of that which reacted) was isomerized into 2-butene, and 2.1% (2.8% of that which reacted) was converted into cracking products ($C_1 + C_2 + C_3$). It will be seen later that a certain amount of butenes and butane were dissolved in the liquid condensate, and when this is taken into consideration it is found that 1-butene reacted to the extent of 74.4%, 8.3% of the original amount (11.2% of that which reacted) was converted into butane, and 12.3% (16.5% of that which reacted) was converted into 2-butene.

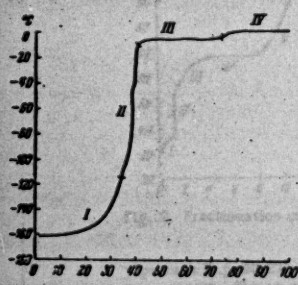

Fig. 1. Fractionation curve for the gaseous reaction products of the hydrocondensation of carbon monoxide with 1-butene (Experiment 306).

Part of the combined liquid condensate from Experiments 306-313 (200 ml) was separated from reaction water, washed twice with 2% caustic soda solution and then with water until neutral, and sealed in an ampoule with anhydrous copper sulfate. After this dehydration treatment, the copper sulfate was filtered off, and the dry condensate was subjected to debutanization in a low-temperature column. A part of the condensate was distilled off below 19°, and this amounted to about 21% by volume of the whole, had p_0 814 mm, and consisted of 31.3% of 1-butene, 49.4% of 2-butene, and 19.3% of butane. After the debutanization, a C_5 fraction (6.3% by volume) was distilled from the condensate through the same column; it came over at 19.5-22° — most of it at 20° — and it had n_D^{20} 1.3639, d_4^{20} 0.6276, and bromine value 184.0, which corresponds to 80.5% of unsaturated hydrocarbons. According to its boiling point and constants (n^{20} and d_4^{20}), this fraction was a mixture of 3-methyl-1-butene (data in literature [10]: b.p. 20.06°, n^{20} 1.3643; d_4^{20} 0.6272) and 2-methylbutane, components which form an azeotrope of b.p. 20° [11]. After debutanization and removal of the C_5 fraction, the condensate had n_D^{20} 1.4190; d_4^{20} 0.7304, and bromine value 59, which corresponds to 52% of unsaturateds. A portion of the condensate (92 ml) was hydrogenated in presence of platinized charcoal to which some chloroplatinic acid had been added [12]. The dry hydrogenation product, which had n_D^{20} 1.4130; d_4^{20} 0.7300, and bromine value 3.3 was fractionated (72 ml was taken) through a 90-plate

TABLE 2

Fraction	B.p. (°C)	Content of fraction in in outgoing gas (%)	Vapor pressure at 9° p_9 (mm)	Composition of fraction		
				gas	(%) on fraction	(% on total outgoing gas)
I	—161 to —115	34.3	—	H_2	58.6	20.0
				CO	15.8	4.4
				CH_4	27.6	9.3
II	—115 to —10	6.4	—	C_2H_4	9.4	0.6
				C_3H_6	44.1	2.8
				$C_3H_6 + C_3H_8$	45.8	2.9
				CO	0.7	0.04
III	—10 to —5	33.3	931	1-Butene	84.4	28.1
				2-Butene	5.8	1.9
				Butane	9.8	3.3
IV	—5 to —2	26.0	794	1-Butene	22.2	6.9
				2-Butene	50.1	11.9
				Butane	27.7	7.2

column, when 35.6% by volume came over below 131°. The fractionation curve is shown in Fig. 2. The residue from this distillation (b.p. above 131°) was distilled from a Favorsky flask. All of the fractions collected and their properties are given in Table 3.

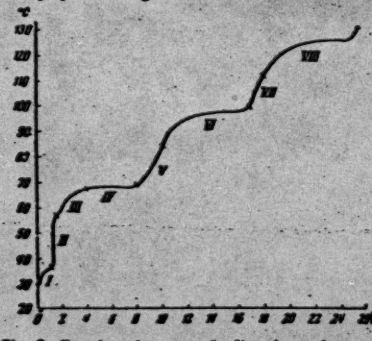

Fig. 2. Fractionation curve for liquid reaction products.

From these results it will be seen that about 40% by volume of the condensate distilled in the range 29.5–160° and contained C_5, C_6, C_7, C_8, and C_9 hydrocarbons in the proportions of about 2.3 : 2.4 : 2.7 : 2.9 : 1.0 (the fraction of b.p. 19.5–22° separated from the condensate before its hydrogenation is included in the C_5 hydrocarbons). As will be seen from Table 3 and Fig. 2, the supplementary C_5 fraction (Fraction I, Table 3), the bulk of which boiled at 36° and had n_D^{20} 1.3568 and d_4^{20} 0.6222, was n-pentane (data from literature [10]: b.p. 36.07°; n_D^{20} 1.3576; d_4^{20} 0.6262), mixed with some 2-methylbutane (b.p. 27.85°; n_D^{20} 1.3537; d_4^{20} 0.6197 [10]). It may be assumed, therefore, that the n-C_5 : i-C_5 ratio in the condensate was about 1 : 4. Fraction III (Table 3) (b.p. 87–88°, n_D^{20} 1.3724; d_4^{20} 0.6538) corresponded most closely in properties to 2-methylpentane (b.p. 60.27°; n_D^{20} 1.3715; d_4^{20} 0.6532 [10]), but it appeared to contain a little n-hexane. Fraction IV (b.p. 68–69°, n_D^{20} 1.3743; d_4^{20} 0.6595) was n-hexane (b.p. 68.74°, n_D^{20} 1.3749; d_4^{20} 0.6594 [10]). The heptane fraction (Fraction VI), which boiled mainly within the limits 95–97° (Fig. 2) and had n_D^{20} 1.3867 and d_4^{20} 0.6830, consisted mainly of n-heptane (b.p. 98.43°, n_D^{20} 1.3877; d_4^{20} 0.6837 [10]); the somewhat low values of the constants must be attributed to some admixture with branched heptanes. Under the conditions of the hydrocondensation reaction, branched hydrocarbons formed will contain, in the main, only one side chain. Hence, for the identity of the admixed substance we can assume only 2-methylhexane, since of the heptane isomers having one methyl side group, only this has lower constants (n_D^{20} 1.3849, d_4^{20} 0.6786 [10]) than n-heptane. Fraction VIII (n_D^{20} 1.3972, d_4^{20} 0.7022) consisted mainly of n-octane (b.p. 125.67°; n_D^{20} 1.3974; d_4^{20} 0.7025 [10]).

When Fractions VIII, VI, and a mixture of Fractions III and IV were investigated by the Raman spectrum method*, only normal C_8, C_7, and C_6 paraffins were detected, characterized respectively by the following wave

* The spectra were determined by Tr. P. Egorov, to whom the authors express their thanks.

numbers (cm^{-1}):

Fraction VIII, 280(4), 813(1b), 860(2), 895(4), 950(1), 1030(3b), 1045(3b), 1060(4b), 1085(4b), 1140(3), 1304(6), 1440(10), 1458(10); Fraction VI, 310(3), 835(2), 905(4), 1045(2b), 1080(4b), 1140(3), 1304(6), 1364(1), 1438(10), 1460(10); Fractions III and IV, 403(2), 825(3), 893(4), 901(4), 1040(4), 1065(1), 1080(2), 1140(2), 1306(6), 1440(10), 1460(10).

TABLE 3

Fraction	Boiling limits (°C)	Content in original condensate (% by volume)	n_D^{20}	d_4^{20}	C_n
I	29,5—36	1,6	1.3568	0.6222	C_5
II	36—57	1,0	1.3628	0.6345	—
III	57—68	4,3	1.3724	0.6523	C_6
IV	68—69	4,3	1.3743	0.6595	C_6
V	69—84	2,8	1.3775	0.6665	—
VI	84—100	9,7	1.3867	0.6830	C_7
VII	100—112	1,5	1.3900	0.6875	—
VIII	112—131	10,4	1.3972	0.7028	C_8
IX	131—160	3,5	1.4073	0.7213	C_9
X	160—178	11,5	1.4113	0.7297	C_{10}
XI	178—200	6,7	1.4152	0.7421	C_{11}
XII	200—220	7,1	1.4208	0.7483	C_{12}
XIII	220—240	7,0	1.4255	0.7578	C_{13}
XIV	240—260	6,1	1.4302	0.7669	C_{14}
XV	260—280	5,0	1.4343	0.7762	C_{15}
XVI	280—310	7,4	1.4382	0.7820	$C_{16,1}$
XVII	310—338	5,0	1.4448	0.7952	$C_{18,1}$
Residue	—	2,2	—	—	—
Original condensate	—	—	1.4130	0.7300	—

Effect of the Concentration of Hydrogen in the Original Mixture on the Course of the Hydrocondensation of Carbon Monoxide with 1-Butene

Comparison of results obtained in this investigation with results obtained previously [2] enables us to draw some conclusions concerning the effect of the concentration of hydrogen in the original gas on the course of the hydrocondensation of carbon monoxide with 1-butene, for the remaining conditions are comparable. The relative amounts of 1-butene and hydrogen in the original gas were about 3.5 : 1 in the present investigation and 1 : 1 in the previous investigation [2]. This change in the ratio of two main components for an unchanged concentration of the third resulted in considerable changes in the course of the reaction as follows. As a result of the 3.5-fold increase in the 1-butene: hydrogen ratio, the total yield of liquid hydrocarbons increased by 50-100% (from 480-650 ml/cu.m or 35-55 ml/liter·hour to 730-975 ml/cu.m or 70-100 ml/liter·hour), the amount of 1-butene that reacted changed from 97% to 76%, the content of unsaturateds in the hydrocondensate rose from 28% to 52%, and the average molecular weight of the hydrocondensate increased. In the previous and present investigations the upper boiling limits of the hydrogenated liquid hydrocondensates were, respectively, 276° and 340°, the contents in these of the C_5 fractions were 24% and 8%, the contents of the C_6 fractions were 15% and 9%, and the yields of butane on the amount of 1-butene that reacted were 32% and 9.4%. As regards the structures of the reaction products, they were found to be the same in both cases, the products being mainly aliphatic hydrocarbons of normal structure, with the exception of the C_5 fractions, which contained isopentane. It is interesting to note that previously, in an investigation of the hydrocondensation of carbon monoxide with ethylene [13], we found that the optimum ratio of ethylene to hydrogen was 2.5-3.

SUMMARY

1. The catalytic hydrocondensation of carbon monoxide with 1-butene was investigated at 190° at

atmospheric pressure. The original gas mixture consisted of 4-6% of carbon monoxide, 70-75% of 1-butene, and 20-25% of hydrogen.

2. The yield of liquid condensate attained 975 ml/cu.m or 100 ml/liter·hour. 1-Butene reacted to the extent of 74.4%, and about 9.4% of the 1-butene that reacted was hydrogenated to butane and about 15% was isomerized into 2-butene.

3. The liquid condensate, after being freed from the C_4 fraction and isopentane, contained 52% of unsaturated hydrocarbons.

4. The presence of up to 25% of 2-butene in the original gas mixture had almost no effect on the yield of liquid condensate in the hydrocondensation of carbon monoxide with 1-butene.

5. After being hydrogenated, the reaction products consisted essentially of saturated normal hydrocarbons containing, apparently, a very small amount of hydrocarbons having one methyl side group on the second atom of the hydrocarbon chain.

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THERMAL REACTIONS OF TETRACHLOROETHYLENE AT SUPERHIGH PRESSURES

M. G. Gonikberg, V. M. Zhulin, and V. P. Butuzov

There have been reports in the literature of two attempts to prepare polymers of tetrachloroethylene by the use of superhigh pressure in conjunction with high temperature. Korshak and Matveeva [1] reported that they did not succeed in effecting the polymerization of tetrachloroethylene under a pressure of 5000 atm and at a temperature of 200°; the paper gives no further details of the results of the investigation. In 1953, Klaasens and Gisolf [2] investigated the mass polymerization of some unsaturated compounds at pressures of up to 10,000 atm. The apparatus described by these authors enabled them to measure the temperature within the mass of compressed material in the pressure vessel; the material was heated electrically by means of a spiral element. The use of such a heating system naturally resulted in considerable overheating in the vicinity of the spiral. The authors reported that at 10,000 atm and 150° tetrachloroethylene is carbonized as a result of a very rapid "explosive" process.

Tetrachloroethylene is a thermally stable compound. Experiments on the decomposition of tetrachloroethylene by the heat from a platinum wire electrically heated to 700-850° [3] showed that in seven hours 25 g of tetrachloroethylene gave 0.5 g of hexachlorobenzene and a very small amount of hexachloroethane. In work on the pyrolysis and chlorinolysis of some unsaturated perchloro hydrocarbons [4] it was found that tetrachloroethylene, unlike hexachloropropene, did not undergo any change in 12-15 seconds at 500°. Under the same conditions in presence of chlorine, hexachloroethane was formed in a yield of about 9% by weight on the amount of tetrachloroethylene taken.

EXPERIMENTAL

The tetrachloroethylene used was distilled through a 20-plate column and was found to have the following constants: b.p. 120.2-120.5° (751 mm); n_D^{20} 1.5057; d_4^{20} 1.6231. The literature [5] gives: b.p. 121.0° (760 mm); Hj_{20} 1.50494*; d_4^{15} 1.63109; d_4^{20} 1.60640.

We investigated the thermal reactions of tetrachloroethylene at pressures of up to 30,000 atm and at temperatures of up to 350°. The very first experiments (25,000 atm, 350°) showed that, under these conditions, tetrachloroethylene is converted into a solid mass consisting largely of hexachloroethane. The experiments were carried out in a superhigh-pressure multiplier with double mechanical support. In this apparatus it was possible to create pressures in the solid and liquid phases of up to 35,000 kg/sq.cm and simultaneously heat substance to 500-550° [6,7]. A heating element was contained in the conical high-pressure vessel, and inside the element was a lead ampoule containing tetrachloroethylene. The pressure was measured potentiometrically by a manganin manometer placed in the lower, cold part of the bore of the high-pressure vessel. The temperature was measured also potentiometrically by a differential iron-nichrome thermocouple and a copper resistance thermometer. The hot junction of the thermocouple was in the pocket of the ampoule (see below); the cold junction was in the lower part of the bore of the pressure vessel (insulated from the heating element by mica strips) inside the resistance thermometer. A four-circuit lead was assembled in the pressure vessel, and connections could be made from the outside to the manganin manometer, the copper resistance thermometer, the heating element, and the thermocouple.

The tetrachloroethylene was contained in a lead ampoule, about 0.5 ml in capacity and having a pocket for the thermocouple in its wall; the ampoule was sealed with lead. The position of the thermocouple made it possible to guard against overheating, which was more difficult to detect when the thermocouple was in

* Calculated from data for 15°.

the stopper of the ampoule as in our previous investigation [8] on the polymerization of 2,3-dimethyl-2-butene under a pressure of 27,500 atm. The use of lead for the construction of the ampoule was determined by its high plasticity and ability to transmit the external pressure satisfactorily. At 20,000 atm the melting point of lead is raised to about 460°, so that it was possible to carry out our experiments at 350°.

We carried out experiments with tetrachloroethylene at 350° (23,000 atm and 2 hours), 316° (24,000 atm and 6 hours), and 300° (22,000 atm and 6 hours, and 10,500 atm and 3 hours). The amount of tetrachloroethylene taken was 0.5-0.8 g. We give a detailed account of the results of the experiments at 350° and 23,000 atm.

A dark-brown solid (0.71 g) was removed from the ampoule. Vacuum distillation (15-17 mm) enabled us to isolate:

a) hexachloroethane (0.31 g, i.e. 44%), m.p. 185.3° after vacuum sublimation (the literature [9] gives m.p. 186.8-187.4°);

Found %: C 9.96, 10.09, 10.06; Cl 89.78, 90.05, 89.98. C_2Cl_6. Calculated %: C 10.15; Cl 89.85.

b) hexachlorobenzene (0.07 g, i.e. 10%), which was recrystallized twice from a benzene-ethanol mixture and vacuum distilled, when it melted at 228° (the literature [9] gives m.p. 227°) and in admixture with known hexachlorobenzene had m.p. 227.6°.

Found %: C 25.18, 25.16; Cl 74.61, 74.76. C_6Cl_6. Calculated %: C 25.23; Cl 74.72.

The residue from the distillation, amounting to 0.09 g (13%), was a resinous substance.

Found %: C 26.32, 26.22; Cl 69.60, 69.62; ash 1.84, 1.40.

Considerable yields of hexachloroethane were obtained also in the experiments at 316° and 300° (40-50%); reaction products included also a small amount of a heavy liquid, which distilled from an Emich tube as a colorless liquid containing hexachloroethane.

We also carried out experiments on tetrachloroethylene in which 4% of benzoyl peroxide (150°; 30,000 atm; 7 hours) or 5.5% of tert-butyl peroxide (200°; 24,700 atm; 6 hours) was present. Neither polymerization products nor thermal-decomposition products were found, the tetrachloroethylene being recovered unchanged.

Hence, we did not succeed in polymerizing tetrachloroethylene under the stated conditions of superhigh pressure and high temperature, a fact that is undoubtedly to be associated with the presence of very considerable steric hindrance. Moreover, in our experiments we did not confirm the findings of Dutch investigators [2] concerning the occurrence of an "explosive" process which results in the carbonization of tetrachloroethylene at 150° and 10,000 atm. We consider that this discrepancy results from local overheating in the experiments of these authors and from poor heat transfer within the bulk of the material under conditions of rapid reaction.

At 300-350° in the pressure range studied (10,500-24,000 atm), tetrachloroethylene undergoes almost complete thermal transformation and it is not possible to determine the effect of pressure on the rate of the process. However, a subsequent investigation at lower pressures has shown that increase in pressure brings about a considerable increase in the rate of the thermal transformations of tetrachloroethylene.

The mechanic M. D. Pushkinsky took part in the work.

SUMMARY

1. The reactions of tetrachloroethylene at 10,000-30,000 atm and 150-350° were investigated in presence and absence of peroxides.

2. Under the conditions studied, tetrachloroethylene does not polymerize. In 2-6 hours at 300-350° it undergoes almost complete thermal transformation with formation of 40-50% of hexachloroethane and a smaller amount of hexachlorobenzene.

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ESTERIFICATION IN PRESENCE OF BORIC ACID, AND THE SYNTHESIS OF BORIC ACID

V. K. Kuskov and V. A. Zhukova

Boric acid is an extremely weak acid. The available data [1,2] indicate that boric acid molecules combine together through hydrogen bonds, so that in structure boric acid is akin to macromolecular compounds. It may be supposed that it is for this reason that the elimination of a proton is difficult and that boric acid - like its dehydration products, "polyboric acids" - is such a very weak acid. It may be supposed also that, under conditions that prevent the association or polymerization of boric aicd or polyboric acids, more definite acidic properties will be found. It is well known that, in presence of monohydric alcohols (glycerol, mannitol), boric acid forms complex compounds that titrate to a phenolphthalein end point as if boric acid were a monobasic acid of medium strength [3]. Boric esters form complex compounds with sodium alkoxides of formula $Na^+[(AlkO)_4B]^-$; these have the properties of salts of a comparatively strong acid [4].

These observations permit us to suppose that, under certain conditions, boric acid (or diboric acid, tetraboric acid, or other dehydration products) will behave as a fairly strong acid. One criterion of the strength of an acid is its activity as a catalyst [5], particularly in esterification reactions. In the present investigation we have found that under conditions under which reaction water is removed - 160-200° - boric acid catalyzes the esterification of carboxylic acids, such as benzoic, phthalic, and adipic acids. For the esterifications we used water-immiscible alcohols, namely, butyl, isobutyl, and isopentyl alcohols. During the reaction the water was distilled over into a water-separation tube, i.e. the reaction was carried out in a Dean and Stark apparatus. The alcohol was added dropwise to the heated mixture of the carboxylic acid and boric acid, the rate of addition being such that the temperature was maintained at about 200°, and not below 160°. When the addition of the alcohol was too rapid, the boiling point of the reaction mixture fell and esterification stopped, as could be readily seen by observing the water-separation tube, in which water ceased to collect. Towards the end of the reaction the boiling point of the reaction mixture fell.

Replacement of boric acid by metaboric acid did not effect any improvement in the reaction. It was evident that, in the last stage of the reaction, boric acids were converted into boric esters; metaborates were not formed. No resinous products were formed in the esterification. It was possible to isolate the required ester by simple distillation of the reaction mixture, for no resinification occurred under these conditions; it was generally difficult, however, to separate this ester from the boric ester, owing to the closeness in boiling point. A wash with water, with weak sodium carbonate solution, and again with water readily removed the easily hydrolyzed boric ester together with any boric and carboxylic acids present. When, owing to the low boiling points of the components, it was impossible to heat the mixture to 160° -- and it is better to heat to 200° - no esterification occurred. For example, we were unable to prepare acetic and butyric esters in presence of boric acid.

We found that, in absence of boric acid, butyl alcohol was not esterified. The esterification of benzoic acid with isopentyl alcohol, which was described by Lacroix and Vigier [6], was only partial - more than one-third of the acid did not react, i.e. the results of these authors were not confirmed. It was further found that boric esters are not intermediaries in the esterification of carboxylic acids in presence of boric acid. When, in fact, boric acid was replaced by its ester, esterification was much slower and was incomplete; also, some trialkyl borate came over with the water and alcohol. This did not occur during esterification in presence of boric acid. It could not be considered also that reaction with dehydration products of boric acid resulted in the formation of a carboxylic anhydride or "mixed" anhydride, which then acylated the alcohol. In a control experiment we heated a mixture of benzoic and boric acids at 200-220° for four hours in the Dean and Stark apparatus. Owing to anhydrization of the boric acid, 0.5 mole of boric acid lost 6.5 ml (about 0.35 mole) of water. Distillation of the reaction mixture remaining in the flask gave benzoic acid, not benzoic anhydride. It is evident that no benzoic anhydride is formed under the conditions of the esterification reaction.

Finally, mixed anhydrides of boric acid and the carboxylic acid do not act as a catalyst in the esterification. This is demonstrated by the following experiment. It has been shown that, when phthalic anhydride is

heated with boric acid, a mixed anhydride "boron phthalate" is formed [7]. Reaction between phthalic anhydride and butyl alcohol in presence of boron phthalate did not proceed readily: monobutyl phthalate was obtained, but very little dibutyl phthalate. On the other hand, when phthalic anhydride was first heated with butyl alcohol, i.e. was converted into monobutyl phthalate, which is unable to form a compound with boric acid, its esterification to dibutyl phthalate in presence of boric acid was found to be quite possible.

By the same method, i.e. heating of the components with distillation of the water formed into a water-separation tube, boric esters were prepared in accordance with the equation:

$$3ROH + H_3BO_3 \rightarrow B(OR)_3 + 3H_2O.$$

Reaction proceeded satisfactorily at 80° and higher. Water was distilled off with the esterifying alcohol, or, when the latter was water-soluble, with specially added benzene, toluene, or xylene. Even tripropyl borate, for which the reaction temperature was 82°, was obtained in high yield. Tributyl borate was formed smoothly; in the distillation reaction water came over with excess of butyl alcohol at 113-125°, or at 80° when benzene was added to the reaction mixture. The synthesis of triisopropyl borate proceeded at 73° (boiling point of the mixture), but the boric acid did not react completely and the yield of ester was only 30%.

The procedure described is convenient as a preparative method. The following methods, which have been proposed previously for the preparation of boric esters, are less convenient and often give poor yields: reaction of alcohols with boric-acetic anhydride [7], boron trichloride [8], boryl sulfate [9], or boric anhydride [10]; esterification in presence of hydrochloric acid [11] or the method of preparing tributyl borate from boric acid and absolute butyl alcohol [12], more recently applied in the preparation of some other boric esters [13].

Our investigation showed that, even at about 80°, boric acid can be esterified and, contrary to statements in the literature [14], the presence of another mineral acid is not necessary. It cannot be supposed that boric acid acts simply as a dehydrating agent, first losing water with formation of metaboric acid or other anhydrization product and then combining with water formed during esterification, etc. The data in the literature [2] shows that boric acid does not lose water below 100°. We found experimentally that, when benzene was boiled over boric acid in a Dean and Stark apparatus (i.e. at 80°), no water came over, but, when butyl alcohol was added to the mixture, esterification very quickly began (at the same temperature of 80°) and reaction water distilled off. It is evident that, in an anhydrous medium at 80° and higher, boric acid is strong enough to catalyze the formation of boric esters. It is most probable that association of boric acid molecules does not occur under these conditions, so that it reacts as a comparatively strong acid. The esterification of carboxylic acids is similarly accelerated, but, as this reaction occurs at 160-200°, it is probable that in this case it is not orthoboric acid that takes part in the reaction, but its anhydrization products. Above 100°, boric acid loses water and is converted, according to available data [2], into pyroboric acid $H_2B_2O_4$, and further — above 140° — into tetraboric acid. It is evident that these are the acids that catalyze the esterification of carboxylic acids.

The electronic structure of boric acid is not inconsistent with these views. The boron atom of boric acid, being surrounded with a sextet of electrons, must have a tendency to confer acid properties. The anion of monomeric metaboric acid should be stabilized as a result of the symmetrically disposed oxygen atoms, as in the acetate and nitrate anions. This should favor the elimination of a proton. In an analogous way the anions of di- and tetra-boric acids may be stabilized.

EXPERIMENTAL

1. Synthesis of Carboxylic Esters

Synthesis of Butyl Benzoate. A mixture of 30.5 g (0.25 mole) of benzoic acid and 3.1 g (0.05 mole) of boric acid was heated to 200° in a three-necked flask fitted with thermometer, dropping funnel, and water-separation tube. The mixture was boiled while 37 g (0.5 mole) of butyl alcohol was added from the dropping funnel over a period of eight hours. About two-thirds of the alcohol was added at 200-205°, and the temperature in the flask then fell — finally to 155°. When water ceased to distil over, the mixture was boiled for a further 30 minutes and cooled. Cold water (25 ml) was added, and the mixture was shaken carefully. The mixture was extracted with 50 ml of benzene, and the water layer containing precipitated boric acid was removed. The benzene layer was washed with 5% sodium carbonate solution and with water, and was then dried with magnesium sulfate. Benzene was distilled off, and the butyl benzoate was distilled (b.p. 247-249°). The yield was 30 g (87.8%).

Synthesis of Dibutyl Phthalate. The same apparatus was used. A mixture of 30 g (0.2 mole) of phthalic anhydride and 25 g (0.33 mole) of butyl alcohol was heated at 200° for two hours. The mixture was cooled to

100°, and 2.5 g (0.04 mole) of boric acid was added. The mixture was then heated to 200° and boiled for 12 hours while 27 g (0.37 mole) of butyl alcohol was added dropwise. After two-thirds of the butyl alcohol had been added, the temperature gradually fell from 200° to 135°. It was then boiled for five hours (until distillation of water ceased completely). The further treatment was as in the preceding experiment. The yield of dibutyl phthalate, b.p. 179-182° (3 mm), was 44.6 g (80%).

Isobutyl benzoate, isopentyl benzoate, and dibutyl adipate were prepared similarly to butyl benzoate. The results are given in Table 1.

TABLE 1

No.	Ester prepared	Amount of boric acid (g)	Amount of alcohol (g)	Reaction temperature (°C)	Time (hours)	Yield of ester (g)	Yield of ester (%)
1	Butyl benzoate	30.5	37	200—130, at end 155	8	39	87.6
2	Isobutyl benzoate	30.5	37	Ditto	10	40	90
3	Isopentyl benzoate	30.5	60	"	5	40	83.3
4	Dibutyl adipate	14.6	37	200—140	10	22	85.3
5	Diburyl phthalate	30	52	200—135	14	44.6	80

2. Synthesis of Boric Esters

Triisopropyl Borate. A mixture of 15.5 g (0.25 mole) of boric acid and 10 ml of benzene was prepared in a flask fitted with dropping funnel, thermometer, water-separation tube, and reflux condenser. A mixture of 60 g (1 mole) of absolute isopropyl alcohol and 30 ml of benzene was placed in the dropping funnel. About one-third of this mixture was run into the flask, and the contents of the flask were boiled for eight hours (b.p. 71-73°). Boiling was then maintained for seven hours while the remainder of the mixture of isopropyl alcohol and benzene was added dropwise. A further 10 ml of benzene and 15 g (0.25 mole) of isopropyl alcohol was then added, and boiling was continued for three hours (73°), until water ceased to separate. The contents of the flask were distilled through a Vigreux column 12 cm in height, and the fraction boiling over 120° (upper limit nearly 150°) was collected. Redistillation of this fraction gave 7 g (30%) of triisopropyl borate, b.p. 125-135° (which corresponds to data in the literature [7]).

Tripropyl Borate. A mixture of 7.75 g (0.125 mole) of boric acid, 30 g (0.5 mole) of propyl alcohol, and 20 ml of benzene was boiled over a sand bath in a flask fitted with a 6-ml water-separation tube and reflux condenser until water ceased to distil off (about eight hours). The boiling point of the mixture was 83°. The further treatment was as for isopropyl borate. The fraction boiling above 160° was collected. Redistillation of this fraction gave 22.4 g (95%) of tripropyl borate, b.p. 177-179° (the literature [7] gives 177°).

A series of boric esters was prepared similarly. Their properties and details of the conditions of synthesis are given in Table 2.

In conclusion, the authors thank S. L. Volkovich for useful suggestions made during this investigation.

SUMMARY

1. It was shown that nonvolatile carboxylic acids can be esterified in presence of boric acids.

2. A method is proposed for the preparation of boric esters.

3. The reactions occuring were investigated experimentally, and theoretical views are advanced on their mechanism.

TABLE 2

No.	Organic radical of boric triester	Alcohol per 0.25 mole (15.5g of boric acid (g)	Auxiliary liquid and its amount (ml)	Reaction temperature (°C)	Time (hours)	Yield (g)	Yield (%)	B.p. in °C (p in mm) Found	B.p. in °C (p in mm) Data from literature
1	Propyl	60	Benzene 40	83	8	22,4	95	177—179	177[7]
2	Isopropyl	75	Benzene 50	73	18	7	30	125—135	125—135[7]
3	Butyl	74	—	113—122	4	55	95,6	230—235	230—235[6]
4	Isobutyl	74	—	114	5	53,5	93		
5	Isopentyl	88	—	124—150	3	64,5	95	252—256	254[6]
6	sec. Octyl	200	—	130—188	3	90	90	180—200(3)	—
7	Cyclohexyl	84	—	220	2	48,5	93	201—203(17)	203(17)[7]
8	Phenyl	75	Toluene 30	126—137	8	64,3	85,4	203—206(3)	
9	Benzyl	81	Benzene 50		6	75	90	220—225(3)	255(17) [7]
10	2-Chloroethyl	71	Benzene 45	108	3	60	94,2	125(5)	*
11	Ethylene (ester with ethylene glycol)	25	Benzene 40	80	7	23,2	92	127—273	272[6]

* Tris-2-chloroethyl borate has not been described in the literature. It is a colorless liquid which darkens in color when kept. It is rapidly hydrolysed by water with separation of boric acid.

Found %: B 4.43, 4.46; Cl 42.91, 42.69. $C_6H_{12}Cl_3O_3B$. Calculated %: B 4.34; Cl 42.82.

[Publisher's Note: Tris-2-chloroethyl borate is, in fact, described by Martin and Mako [8] and by Jones et al. (J. Chem. Soc. 1946, 824).]

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BRIEF COMMUNICATIONS

BREAKDOWN OF THE FERROCENE NUCLEUS BY HYDROGENATION AND THE ACTION OF HALOGENS

A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina, and N. A. Simukova

The study of the laws governing the replacement of the hydrogens of ferrocene (dicyclopentadienyliron) [1] and its derivatives demands the development of a method for proving the structures of di- and poly-substituted ferrocenes [2]. The method of confirmatory synthesis from the corresponding substituted cyclopentadienes, carried out by Pauson [3] for di- and poly-phenylferrocenes and 1,1'-bisdiphenylmethylferrocene, is of little value for this purpose, not only because of the poor accessibility of cyclopentadiene derivatives, but also because the method is applicable only to the preparation of derivatives with hydrocarbon substituents. The most suitable method for proving the structures of polysubstituted ferrocenes depends on the rupture of the iron-carbon bond with formation of cyclopentane derivatives, this being effected by, for example, hydrogenation or the action of halogens. Woodward and coworkers [4] showed that ferrocene is not hydrogenated over reduced platinum oxide under normal conditions. Fischer [5] did not succeed in hydrogenating ferrocene in presence of a nickel catalyst at 150° and 150 atm.

In the present investigation we effected the breakdown of ferrocene and some of its derivatives by the action of bromine and chlorine and by hydrogenation with hydrogen in presence of Raney nickel under severe conditions.

EXPERIMENTAL

Ferrocene (30 g) was hydrogenated in cyclohexane (60 ml) in presence of Raney nickel in a rotating 500-ml autoclave for five hours at 300° and a further four hours at 340°. The initial hydrogen pressure was 120 atm, and the working pressure was 280 atm. Distillation through a 35-plate column gave 4.1 g of cyclopentane, b.p. 47-49° (745 mm), n_D^{20} 1.4060, and d_4^{20} 0.7440, and 3 g of a mixture of b.p. 36-47° (745 mm) and n_D^{20} 1.4040, which, judging from its refractive index, consisted of cyclopentane and 5% of n-pentane [6]. For cyclopentane the literature [6] gives b.p. 48.7-48.8° (742.6 mm), n_D^{20} 1.4060, and d_4^{20} 0.7450. Some ferrocene (16.2 g) was recovered unchanged. The total yield of cyclopentane was 7 g (67% on the amount of ferrocene that reacted).

The yield of n-pentane was increased to 23% on the total amount of cyclopentane when freshly prepared Raney nickel was used. Reduction of the working pressure to 180 atm also increased the yield of n-pentane (to 7% of the total amount of cyclopentane), which is in accord with the results of Kazansky and Terentyeva [7], who showed that with increase in the pressure of hydrogen there was a rise in the temperature at which scission of the cyclopentane ring occurred in presence of a platinum or nickel catalyst.

Diacetylferrocene (28 g) was hydrogenated in alcohol (60 ml). The initial hydrogen pressure was 95 atm, and the working pressure was 240 atm. Heating was for one hour at 100°, two hours at 300°, and five hours at 345°. The products isolated were 9.2 g (53%) of ethylcyclopentane (distilled through a 35-plate column), b.p. 101.3-102.3°, n_D^{20} 1.4202, and d_4^{20} 0.7856, and 3.6 g (15% on the diacetylferrocene taken) of diethylferrocene [8]. For ethylcyclopentane the literature gives b.p. 100.5-101.5° (740 mm); n_D^{20} 1.4202; d_4^{20} 0.7654 [9]; b.p. 101-102° (747 mm) n_D^{20} 1.4200; d_4^{20} 0.7682 [10].

Ferrocenedicarboxylic acid was hydrogenated in the form of a solution of its sodium salt (4.3 g) in water (50 ml) for one hour at 180° and 2.5 hours at 265°. The initial hydrogen pressure was 122 atm, and the working pressure was 280 atm. The produce isolated was 2 g (65%) of cyclopentanecarboxylic acid, identified by

its p-bromophenacyl ester, which melted, both alone and in admixture with an authentic sample, at 75-76°.

When ferrocenedicarboxylic acid was hydrogenated in cyclohexane (five hours at 265° and 200 atm), 37% of cyclopentane and a little ferrocene was obtained. Hydrogenation in alcoholic solution (30 g in 100 ml) resulted in the formation of cyclopentanecarboxylic acid (3.5 g, i.e. 14%) and its ethyl ester (5.2 g, i.e. 17%), b.p. 168.5-170°, n_D^{20} 1.4362, and d_4^{20} 0.9504. For ethyl cyclopentanecarboxylate the literature [11] gives: b.p. 171.9° (737 mm); 89.3° (45 mm); n_D^{20} 1.4360, d_4^{20} 0.9523.

Bis-p-nitrophenylferrocene (12 g) was hydrogenated in cyclohexane (130 ml) for one hour at 142°, three hours at 195°, one hour at 250°, and three hours at 326°. The initial hydrogen pressure was 120 atm, and the working pressure was 280 atm (if the autoclave was heated rapidly, there was an explosion). The product isolated was 1.3 g (15.3%) of cyclopentylcyclohexane, b.p. 75-76° (6 mm), n_D^{21} 1.4750 and d_4^{21} 0.8818. For cyclopentylcyclohexane the literature gives: b.p. 214°; 225-227°, n_D^{21} 1.4728, 1.4767; d_4^{21} 0.8780, 0.8813 [12,13].

Apart from cyclopentylcyclohexane, an appreciable amount of light-brown resin was formed; this substance was insoluble in water and in ether, but soluble in chloroform; it contained nitrogen and iron and rapidly underwent change in the air. The yield of cyclopentylcyclohexane could not be increased, and resin formation could not be reduced, by more prolonged hydrogenation (there are references in the literature to difficulties met in the hydrogenation of aromatic amines in presence of Raney nickel [14]).

Thus, the formation of ethylcyclopentane, cyclopentanecarboxylic acid, and cyclopentylcyclohexane by the hydrogenation of diacetylferrocene, sodium ferrocenedicarboxylate, and bis-p-nitrophenylferrocene, respectively, provides the first chemical proof that in these compounds the substituents are in different rings of the ferrocene nucleus.

We effected the breakdown of the ferrocene nucleus also by means of bromine and chlorine. We have previously reported that treatment of ferrocene with bromine in boiling carbon tetrachloride gives pentabromocyclopentane [15]. When ferrocene (1 mole) was treated with bromine (6.5 moles) in boiling carbon tetrachloride, a 70% yield was obtained of pentabromocyclopentane, m.p. 103-104° (crystallized from alcohol and carbon tetrachloride). When the amount of bromine or the duration of heating was increased, the yield of pentabromocyclopentane was increased to 80-82%, but a mixture of stereoisomers, m.p. 83-101°, was formed.

Found %: C 13.39, 13.30; H 1.09, 1.08; Br 85.75 85.52. $C_5H_5Br_5$. Calculated %: C 12.92; H 1.08; Br 85.96.

Breakdown of the ferrocene nucleus can be effected also by means of chlorine. Chlorine was passed at room temperature into a solution of ferrocene (1.86 g) in carbon tetrachloride (40 ml) for two hours, and pentachlorocyclopentane was obtained in 62% yield on the amount of ferrocene that reacted (3% of ferrocene remained in the form of a cation). It was found that the yield of pentachlorocyclopentane was raised to 90% by gradually adding a solution of 3.72 g of ferrocene in carbon tetrachloride (20 ml) to an ice-cold saturated solution of chlorine in carbon tetrachloride (80 ml) and then passing chlorine at 0° for two hours. Pentachlorocyclopentane crystallizes from 70% alcohol and can be readily sublimed in a vacuum; m.p. 38-39°.

Found %: C 24.72, 24.66; H 2.17, 2.20. $C_5H_5Cl_5$. Calculated %: C 24.76; H 2.08.

Ferrocene is stable to the action of iodine. After a solution of ferrocene and iodine in acetic acid had been boiled for one hour, the ferrocene was recovered unchanged (the ferrocene-iodine complex was reduced with sodium thiosulfate).

The bromine method of breaking down the ferrocene nucleus was applied to ferrocenecarboxylic and ferrocenedicarboxylic acids. Treatment of ferrocenecarboxylic acid with bromine (boiling for one hour in carbon tetrachloride) resulted in its complete breakdown with formation of a mixture of pentabromocyclopentane isomers, m.p. 80-100°, in 44% yield (an isomer of m.p. 103-104° was isolated after one chromatographic treatment on silica gel) and also a bromine-containing carboxylic acid which decomposed when heated to 90° with gas evolution and blackening. This substance was readily soluble in ether, alcohol, and benzene, but insoluble in petroleum ether; its structure was not established.

Found %: C 25.80, 25.80; H 1.98, 2.15; Br 62.81, 62.96.

When ferrocenedicarboxylic acid was broken down with bromine, only the above-described bromine-containing carboxylic acid was isolated. No pentabromocyclopentane could be detected, even when the reaction product was subjected to chromatographic separation.

Thus, the results of the breakdown of ferrocenedicarboxylic acid with bromine confirm the conclusion drawn from the hydrogenation experiments, namely, that the carboxy groups are in different rings.

One of us, in collaboration with N. A. Volkenau, has effected the breakdown of ethylferrocene with bromine, and pentabromocyclopentane, m.p. 103-104°, was isolated from the products. Breakdown of the ferrocene nucleus with bromine can be applied in the proof of the presence of an unsubstituted ring in a ferrocene dreivative. This method, unlike the hydrogenation method, does not require large amounts of material, since pentabromocyclopentane can readily be isolated chromatographically.

SUMMARY

1. It was shown that ferrocene and its derivatives are broken down with formation of cyclopentane and its derivatives when treated with bromine and chlorine, and also with hydrogen under severe conditions in presence of Raney nickel.

2. It was proved by hydrogenation that the substituents in diacetylferrocene, ferrocenedicarboxylic acid, and bis-p-nitrophenylferrocene are in different rings.

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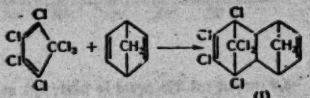
PREPARATION OF BICYCLO[2.2.1]HEPTA-2,5-DIENE BY THE CONDENSATION OF CYCLOPENTADIENE WITH ACETYLENE

A. F. Plate and M. A. Pryanishnikova

Much interest has been shown recently in aldrin, a new, highly effective preparation for the combating of agricultural pests, notable for its high toxicity to insects and its harmlessness to plants.

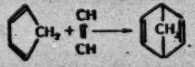
Aldrin (I) (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene) can be prepared by the condensation of hexachlorocyclopentadiene with bicyclo[2.2.1]hepta-2,5-diene [1]:



(I)

Bicyclo[2.2.1]hepta-2,5-diene has been prepared in 25% yield by the elimination of hydrogen chloride from 5-chlorobicyclo[2.2.1]hept-2-ene and the elimination of chlorine from 5,6-dichlorobicyclo[2.2.1]hept-2-ene [2]. Also, its preparation by the condensation of acetylene with cyclopentadiene in 32% yield has been described in a patent [3].

In view of the importance of aldrin, in 1955 we carried out experiments on the condensation of cyclopentadiene with acetylene under pressure at various temperatures in an autoclave:



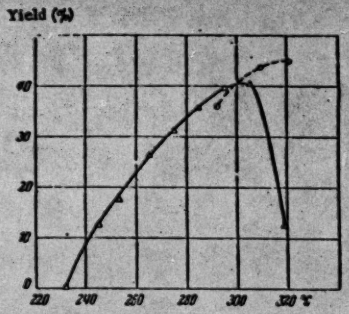
At 290-320° a 40-45% yield of bicyclo[2.2.1]hepta-2,5 diene was obtained. In work at the Ya. V. Samsolov Scientific Institute for Fertilizers and Insectofungicides, aldrin was synthesized from our preparation by condensing it with hexachlorocyclopentadiene [4].

EXPERIMENTAL

Experiments on the preparation of bicyclo[2.2.1]hepta-2,5-diene were carried out in a one-liter rotating steel autoclave placed in an electrically heated furnace. Cyclopentadiene (20 g) and isopentane (20 ml) were loaded into the autoclave, which was then closed. Acetylene was passed in up to a pressure of 9-10 atm, and the autoclave was heated to the required temperature, which was maintained for 5-60 minutes. The maximum pressure attained was not greater than 30 atm. When the autoclave was cool, it was unloaded and the reaction mixture was fractionated. The bicyclo[2.2.1]hepta-2,5-diene then obtained had the following properties: b.p. 89.5-90.5°; n_D^{20} 1.4693, d_4^{20} 0.9056. The literature gives: b.p. 89-89.5°; n_D^{20} 1.4670; d_4^{20} 0.8992 [2]; b.p. 83-86° (620-635 mm); n_D^{20} 1.4685-1.4720; d_{20} 0.8770-0.9100 [3].

The dependence of the yield of bicyclo[2.2.1]hepta-2,5-diene on the reaction temperature and the duration of heating is shown in the diagram. It will be seen that, when heating is for 30 minutes, the diene synthesis between cyclopentadiene and acetylene does not go below 230°. With rise in temperature the yield of

bicyclo[2.2.1]hepta-2,5-diene gradually increases and attains a maximum of 40% at 295-305°. With further rise in temperature the yield of the desired product falls rapidly as a result of the resinification of the reaction products.



Relation between the yield of bicyclo[2.2.1]hepta-2,5-diene and the temperature: _____ duration of heating 30 minutes; _____ duration of heating 5 minutes.

However, when the heating is for a shorter time the optimum temperature for the reaction appears to be higher. Thus, reaction at 320° for five minutes resulted in a 45% yield of bicyclo[2.2.1]-hepta-2,5-diene. The investigation is continuing.

SUMMARY

The condensation of cyclopentadiene with acetylene under pressure gave a 40-45% yield of bicyclo[2.2.1]hepta-2,5-diene, the starting material for the synthesis of the insecticide aldrin.

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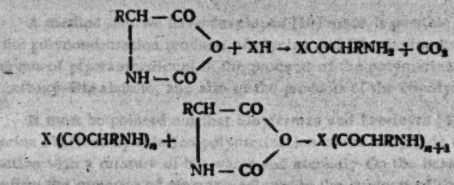
SOME PECULIAR FEATURES OF THE POLYMERIZATION OF ANHYDRIDES OF α-CARBOXYAMINO ACIDS

K. T. Poroshin

Much attention hasbeen devoted recently to the synthesis of polyanhydro-α-amino acids and the study of their properties, for these compounds are to a certain extent analogous to the simplest proteins and to certain antibiotics and hormones. Apart from the polycondensation of esters of α-amino acids, considerable progress has been made in the investigation of the polymerization of anhydrides of α-carboxyamino acids [1]. For a long time many investigators [2] adopted the view that the mechanism of the polymerization Reaction (1) consisted in the initiation and propagation of this reaction and that the polypeptides formed cannot react among themselves after the whole of the α-carboxyamino acid anhydride has been used up:

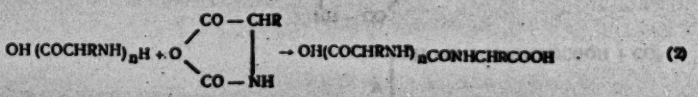


$$X(COCHRNH)_n + \text{(NCA)} \rightarrow X(COCHRNH)_{n+1} + CO_2, \qquad (1)$$

in which X = OH, R_2N, OR (initiators).

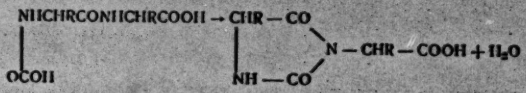
Water, amines, and alcohols can serve as initiators. When water is used as an initiator, the polyanhydro-α-amino acids obtained by the polymerization of α-carboxyamino acid anhydrides should contain equal numbers of carboxyls and terminal amino groups. However, it was shown by Sela and Berger [3] and by Sluyterman and Labrieyre [4] that the carboxyl content of the polyanhydro-α-amino acid is higher than that indicated by Equation 1.

Sela and Berger [3] suggested that, in addition to the main Reaction (1), the Process (2) may occur, i.e. the amino group of the peptide may react with the second carbonyl group of the α-carboxyamino acid anhydride with formation of a compound with a free carboxyl group:



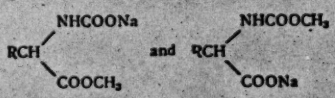
$$OH(COCHRNH)_nH + \text{(NCA)} \rightarrow OH(COCHRNH)_nCONHCHRCOOH \qquad (2)$$

Hence, if Reaction (2) occurs, "urea-peptides" may be formed, and these may yield the hydantoin of the amino acid or of the peptide, e.g.



Wessely and Mayer [5], and also Granacher and Wolf [6] isolated the corresponding hydantoins from polypeptides obtained from anhydrides of α-carboxyamino acids.

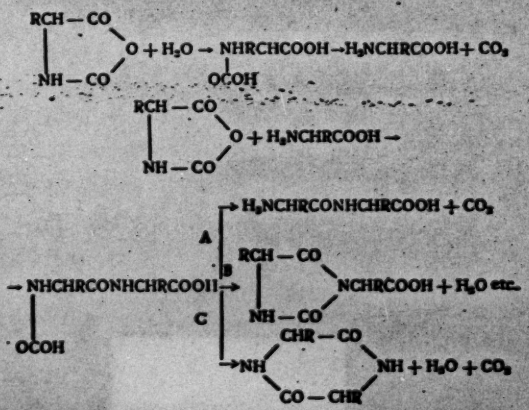
Substantial proof of the possibility of a reaction of Type (2) is provided by the investigations of Berger, Sela, and Katchalski [7] and of Farthing [8], who showed that an anhydride of an α-carboxyamino acid can react with sodium methoxide in presence of methanol with formation of both the sodium salt of methyl 2-(carboxyamino) alkanoate (main reaction) and also the sodium salt of 2-(methyoxycarbonylamino)alkanoic acid, i.e.



In this connection the work of Frenkel, Neufeld, and Katchalski [9] is deserving of attention.

A method that we have developed [10] made it possible to determine the amount of 2,5-piperazinediones in the polycondensation products of glycine and DL-alanine esters. Applying this method, we determined the amounts of piperazinediones in the products of the polymerization of the anhydrides of N-carboxyglycine and N-carboxy-DL-alanine, and also in the products of the copolymerization of these anhydrides.

It must be pointed out that Sluyterman and Labrieyre [4] isolated about 2% of piperazinediones from polyglycine obtained by solution polymerization of the anhydride of N-carboxyglycine, this being effected by extraction with a mixture of hot water and alcohol. On the basis of this fact— and also of our own results, which confirm the presence of piperazinediones in the products of the polymerization of anhydrides of α-carboxyamino acids — it may be assumed that, in addition to the main reaction of linear-polymer formation and the reaction in which "hydantoin-peptides" are formed, a process occurs in which piperazinediones are formed. In view of these considerations, the polymerization reaction of α-carboxyamino acid anhydrides can be considered to occur by the following mechanism:



We must point out that, under certain conditions of temperature, the possibility cannot be excluded of the formation of piperazinediones directly from dipeptides[11].

EXPERIMENTAL

The anhydrides of N-carboxyglycine and N-carboxy-DL-alanine were prepared from the benzyloxycarbonyl derivatives of the amino acids. N-(Benzyloxycarbonyl) glycine was prepared by the gradual addition (over a period of 10-15 minutes) of 21 g of benzyl chloroformate and 25 ml of 4 N NaOH to a solution of 7.5 g of glycine in 50 ml of 2 N NaOH. Reaction proceeded in the cold for 30-40 minutes. The solution was washed twice with ether, and the aqueous solution was then acidified to Congo red with concentrated sulfuric acid. The precipitated crystals of N-(benzyloxycarbonyl)glycine were washed with water. Recrystallization was not generally necessary, satisfactory analytical results being obtained on the original product:

Found %: C 57.42; H 5.37; N 6.64. $C_{10}H_{11}O_4N$. Calculated %: C 57.39; H 5.30; N 6.70.

The molecular weight of the N-(benzyloxycarbonyl)glycine was 209.1, and it melted at 120°.

N-(Benzyloxycarbonyl)-DL-alanine was prepared by the same method. Benzyl chloroformate (24 g) and 4 N NaOH (25 ml) were added in portions to a solution of 8.9 g of DL-alanine in 50 ml of 2 N NaOH. After the first crystallization the compound melted at 114° and had a molecular weight of 223.1. The elementary analysis was as follows:

Found %: C 59.20; H 5.85; N 6.32. $C_{11}H_{13}O_4N$. Calculated %: C 59.16; H 5.87; N 6.28.

The anhydrides of N-carboxyglycine and N-carboxy-DL-alanine were prepared as follows: the benzyloxycarbonyl derivatives of the amino acids were converted into acid chlorides by treatment with phosphorus pentachloride in ether; benzyl chloride was then eliminated. The anhydrides so formed were crystallized. For the anhydride of N-carboxyglycine:

Found %: C 35.75; H 3.01; N 13.8. $C_3H_2O_3N$. Calculated %: C 35.6; H 2.9; N 13.8.

For the anhydride of N-carboxy-DL-alanine:

Found %: C 41.9; H 4.55; N 12.35. $C_4H_5O_3N$. Calculated %: C 41.7; H 4.3; N 12.2.

The anhydrides of α-carboxyamino acids were polymerized in the mass at reduced pressure (10-12 mm). In all cases water was used as initiator. When the polymerization was complete, the polyanhydro-α-amino-acid (polyglycine, poly-DL-alanine, or the copolymer obtained from a 1 : 1 mixture of the anhydrides of the N-carboxy derivatives of the two amino acids – was carefully washed with absolute ether and subjected to analysis for piperazinedione content by the method that we have developed [10]. The results of the investigation are given in the table, which gives the polymerization conditions (temperature and time), the degree of polymerization n, and the piperazinedione contents of the polyanhydro-α-amino acids obtained.

Name of the polyanhydro-α-amino-acid	Polymerization conditions		n	Piperazinedione content (%)
	Temperature (°C)	Time (hours)		
Polyglycine	100	3	6	13,03
	165	2	10	9,25
	160	2	45	5,39
Poly-DL-alanine	150	2	12	18,38
	100	2,5	14	5,02
	100	4	20	2,34
Glycine-DL-alanine copolymer	105	5	10	6,48
	95	4	34	1,65
	160	2	58	0,37

SUMMARY

1. Polymerization reactions were carried out with anhydrides of N-carboxyglycine and N-carboxy-DL--alanine, and the 2,5-piperazinediones present in the polymerization products were determined quantitatively.

2. A hypothesis is advanced concerning the mechanism of the polymerization reaction of anhydrides of α-carboxyamino acids; it accounts for the formation of 2,5-piperazinediones.

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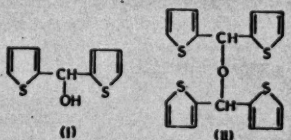
* T.p. = C. B. Translation pagination.

DI-2-THIENYLMETHANOL

Ya. L. Goldfarb and M. L. Kirmalova

As is well known, in the course of its development the chemistry of thiophene has in many respects repeated the chemistry of benzene; this applies both to the substances synthesized and to the methods of synthesis. It is not clear, therefore, why the thiophene analog of such a simple and accessible compound as benzhydrol has not been described (we have been unable to find reports of this substance in the available literature). It is possible that the labile character of di-2-thienylmethanol (I) (see below) is in part responsible for this situation; in this respect it is similar to tri-2-thienylmethanol, which has been isolated only in the form of salts [1], and differs from the comparatively stable alkyl(and aryl)thienylmethanols.

As a part of our laboratory's program of work on the synthesis of di-2-thienylmethane derivatives, we attempted to prepare di-2-thienylmethanol by the usual organomagnesium synthesis, as described for α-methyl-2-thiophenemethanol [2] and α-phenyl-2-thiophenemethanol [3]. Under these conditions, however, reaction was accompanied by considerable resinification, and only the ether (II) was isolated in very small amount. We succeeded in obtaining the alcohol itself by modifying the conditions somewhat, namely, carrying out the synthesis in an atomsphere of nitrogen and decomposing the organomagnesium complex not with acid, but – as is quite customary – with ammonium chloride solution. When the alcohol (I) is heated in a water bath for five minutes in presence of traces of acid, it is converted into the ether (II), the reaction being accompanied by considerable resinification. Work on the properties and reactions of di-2-thienylmethanol is continuing..



(I) (II)

EXPERIMENTAL

Preparation of the ether (II). An ethereal solution of 2-thienylmagnesium bromide prepared from 8.2 g of 2-bromothiophene and 1.2 g of magnesium was added dropwise to a stirred ice-cold solution of 5.6 g of 2-thiophenecarboxaldehyde in 10 ml of dry ether. The yellow precipitate that formed was decomposed under ice cooling with 14 ml of dilute (1 : 1) hydrochloric acid. The dark-colored ethereal solution was separated, washed with sodium bisulfite solution and with water, and dried with magnesium sulfate. After removal of ether a dark-colored crystallizing oil remained. The substance was washed with alcohol and dissolved in hot ligroin. The solution was cooled and gave 1.4 g of a crystalline precipitate, m.p. 79°. After being recrystallized from ligroin and alcohol, the ether melted at 81.5-82.5°. It darkened in color when kept in the cold.

Found %: C 57.85, 57.69; H 3.81, 3.79. $C_{18}H_{14}OS_4$. Calculated %: C 57.72; H 3.77.

Preparation of di-2-thienylmethanol (I). A solution of 8.4 g of 2-thiophenecarboxaldehyde in 20 ml of ether was added with cooling (0-5°) to an ethereal solution of 2-thienylmagnesium bromide prepared from 12.8 g of 2-bromothiophene and 1.9 g of magnesium. The reaction was carried out in an atmosphere of nitrogen. When the addition was complete, stirring was continued for 20 minutes. The precipitate that formed was

decomposed under cooling with 40 ml of concentrated ammonium chloride solution. The ether layer was separated and dried with magnesium sulfate. After evaporation of ether, 12.3 g of a light-colored oil remained, and this crystallized when cooled. A small portion of the crystals was pressed off on a porous tile and recrystallized twice from ligroin: m.p. 56-57°. Di-2-thienylmethanol becomes yellow when kept in the cold.

Found %: C 55.44, 55.35; H 4.06, 3.99. $C_9H_8OS_2$. Calculated %: C 55.07; H 4.11.

SUMMARY

The syntheses are described of the previously unknown di-2-thienylmethanol and bis(di-2-thienylmethyl) ether.

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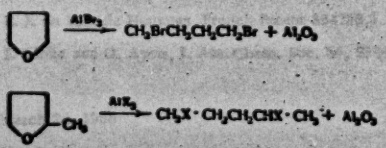
OPENING OF THE TETRAHYDROFURAN RING UNDER THE ACTION OF ALUMINUM HALIDES

N. I. Shuikin and I. F. Belsky

Investigations by various authors have shown that that the tetrahydrofuran ring can be opened under the action of hydrogen halides with formation of the corresponding aliphatic halogen compounds. For example, Froebe and Hochstatter [1] obtained 1,4-dichloropentane by heating tetrahydro-2-methylfuran with concentrated hydrochloric acid in a sealed tube at 60° for four hours.

Starr and Hixon [2] showed that reaction of tetrahydrofuran with dry hydrogen chloride resulted in the formation of 4-chloro-1-butanol in 56% yield. This result was confirmed by Fried and Kleen [3], who studied the action of dry hydrogen halides on tetrahydrofuran and tetrahydro-2,5-dimethylfuran and found that the tendency for the rings of these compounds to open diminishes progressively as we pass from HI to HBr and HCl. The action of dry hydrogen iodide and hydrogen bromide on tetrahydrofuran gave, respectively, 1,4-diiodobutane and 1,4-dibromobutane in yields of 75% and 60%. Reaction of the same hydrogen halides with tetrahydro-2,5-dimethylfuran gave 2,5-diiodo- and 2,5-dibromohexanes. Dry hydrogen chloride did not react at all with tetrahydro-2,5-dimethylfuran, but it reacted with tetrahydrofuran with opening of the ring and formation of 4-chloro-1-butanol, in agreement with the results of Starr and Hixon. In the same investigation, Fried and Kleen showed that, in presence of anhydrous zinc chloride, tetrahydrofuran reacted with dry hydrogen chloride with formation of 1,4-dichlorobutane in 56% yield, but tetrahydro-2,5-dimethylfuran gave 2,5-dichlorohexane in a yield of only 8%. French Patent 864759 [4] reports the preparation of 1,5-dihalobutanes in high yields (up to 95%) by the treatment of tetrahydrofuran with hydrogen halides in presence of sulfuric acid or other dehydration catalysts. Cloke and Ayers [5] showed that phosphorus tribromide, like hydrogen bromide, has a splitting effect on the tetrahydrofuran ring: reaction of phosphorus tribromide with tetrahydrofuran results in the formation of 1,4-dibromobutane in 53% yield.

In our investigation we have studied the action of anhydrous aluminum halides ($AlCl_3$ and $AlBr_3$) on tetrahydrofuran and tetrahydro-2-methylfuran. We have showed that under the action of these salts the tetrahydrofuran ring is opened with formation of dihalo paraffins. Tetrahydrofuran and aluminum chloride gave 1,4-dichlorobutane, and with aluminum chloride and bromide tetrahydro-2-methylfuran gave 1,4-dichloro- and 1,4-dibromo-pentanes, respectively.



(X is Cl or Br)

EXPERIMENTAL

Tetrahydrofuran and tetrahydro-2-methylfuran were prepared by the hydrogenation of furan and 2-methylfuran, respectively, over Raney nickel at 125°. They were isolated from the reaction products by fractionation through a 30-plate column. The tetrahydrofuran had b.p. 65-66° (755 mm), d_4^{20} 0.8886, and n_D^{20} 1.4078. The tetrahydro-2-methylfuran had b.p. 79-79.2° (750 mm), d_4^{20} 0.8582, and n_D^{20} 1.4060.

Experiments on the reactions of tetrahydrofuran and tetrahydro-2-methylfuran under the action of aluminum halides were carried out as follows. One molecular proportion of the tetrahydrofuran was introduced into an ice-cooled flask fitted with mechanical stirrer. Not less than two-thirds of a molecular proportion of anhydrous aluminum halide was then added in small portions under constant stirring. Reaction was vigorous and exothermic. After the whole of the aluminum halide had been added, the reaction mixture was stirred for one hour at room temperature and then for 2-3 hours in a water bath. Toward the end of the reaction the mixture became thick and black. The reaction products were extracted with ether, and the ether extract was washed with water and dried with calcium chloride. It was then vacuum fractionated. From the products formed by reaction between tetrahydrofuran and aluminum chloride, we isolated 1,4-dichlorobutane in 32% yield; it had the following properties: b.p. 81-83° (10 mm) d_4^{20} 1.1101; n_D^{20} 1.4590; found MR 30.80, calculated ($C_4H_8Cl_2$)MR 30.41.

Scission of tetrahydro-2-methylfuran by aluminum chloride and bromide under the same conditions gave 1,4-dichloro- and 1,4-dibromo-pentanes respectively. 1,4-Dichloropentane, obtained in 58% yield, had the following properties; b.p. 53-54° (4 mm); 104-105° (115 mm); 162-164° (750 mm); d_4^{20} 1.0731; n_D^{20} 1.4510, found MR 35.39, calculated ($C_5H_{10}Cl_2$)MR 35.02. 1,4-Dibromopentane (67% yield) had the following properties: b.p. 66-67° (6 mm); d_4^{20} 1.6871; n_D^{20} 1.5094; found MR 40.73; calculated ($C_5H_{10}Br_2$)MR 40.82.

Apart from these compounds, reaction of tetrahydrofuran and of tetrahydro-2-methylfuran with aluminum chloride and with aluminum bromide gave some high-boiling halogen-containing substances. For example, from the products of reaction between tetrahydro-2-methylfuran and aluminum chloride we isolated a fraction having the following properties: b.p. 124-127° (10 mm), d_4^{20} 1.0253; n_D^{20} 1.4647; found MR 58.85; calculated ($C_{10}H_{20}Cl_2$)MR 58.12. This fraction appeared to consist essentially of dichlorodecane.

SUMMARY

1. It was shown that the tetrahydrofuran ring is opened under the action of aluminum chloride or bromide with formation of dihalo paraffins.

2. It was found that reaction of tetrahydrofuran with aluminum chloride gives 1,4-dichlorobutane in 32% yield, and reaction of tetrahydro-2-methylfuran with aluminum chloride and with aluminum bromide gives, respectively, 1,4-dichloropentane in 58% yield and 1,4-dibromopentane in 67% yield.

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CURRENT EVENTS

ANNUAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R

The Annual Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR was held on January 31 and February 1, 1956. The Academician-Secetary of the Division of Chemical Sciences, M. M. Dubinin, presented his report on the scientific activities of institutes of the Division during 1955 and the applications made of the Division's work in the national economy.

At the beginning of his address, Academician M. M. Dubinin pointed out that the Annual Meeting was taking place during an important period for the country, on the eve of the Twentieth Congress of the Communist Party of the Soviet Union and soon after the publication of the draft of the Directive of the Congress on the Sixth Five-year Plan for the Development of the National Economy of the USSR (1956-1960). The draft of this directive, stated Academician Dubinin, refers to the world-wide development of science and the extension of theoretical investigations into all branches of knowledge. It is proposed to direct the efforts of scientists and the use of the material resources of scientific institutes onto work mainly concerned with problems of great importance for the national economy. M. M. Dubinin enumerated the problems which came within the responsibility of the Division of Chemical Sciences. In 1955 the activities of the newly created scientific councils and commissions on various problems developed greatly, particularly with respect to the organization of conferences on individual scientific subjects and the examination of matters relating to the organization of scientific work.

Passing to the activities of institutes of the Division during 1955, Academician M. M. Dubinin stated that in the N. S. Kurnakov Institute of General and Inorganic Chemistry work had carried on along lines traditional for that institute. As a result of an investigation on the complex compounds of bi- and quadri-valent platinum, new data had been obtained for the quantitative characterization of the trans effect. With the laws of the trans effect as guide, about forty complex compounds of platinum, palladium, rhodium, iridium, ruthenium, and silver were synthesized. The results of these investigations are of great importance for the preparation of these elements in the pure state. Physicochemical investigations on the simple and complex compounds of germanium, zirconium, hafnium, titanium, neodymium and samarium, tantalum, indium, gallium, thallium, and rhenium have enabled the conditions under which they react with salts, oxides, acids, etc. to be determined. New data have been obtained which are of importance for the preparation of rare elements from Soviet raw materials. The speaker referred also to the work of the institute on natural salts and synthetic inorganic compounds.

Refering to the work of V. G. Khlopin Radium Institute, Academician Dubinin stated that, in development of the fundamental ideas of V. G. Khlopin, investigations have been carried out on the distribution of various new radioactive elements between solids and liquids, and also between two liquid phases. A study was made of the behavior of transuranic elements when precipitated by means of lanthanum potassium double sulfate, and also of the mechanism by which they were entrained. The state of radioactive elements in extremely dilute solutions was studied. Closely agreeing results were obtained by various methods for the uranium contents of stone and iron meteorites; the comparative migration of thodium isotopes from uraninites was studied. The thorough investigation of radioactive methods for the determination of geological age and the improvement of their accuracy was continued.

The interaction of 400-700 Mev particles with complex nuclei was investigated by the method of thick-layer photographic plates. New data were obtained on the mechanism of fission processes at high energies. Progress was made in investigations on nuclear spectroscopy. With the aid of γ-spectrometers of high resolving power constructed at the Institute, the γ-spectra of individual isotopes of lanthanum, gold, iridium,

europium, arsenic, ruthenium, and antimony were investigated, and this made it possible greatly to increase the accuracy of the schemes of energy levels for these elements.

Passing to the activities of the V. I. Vernadsky Institute of Geological and Analytical Chemistry, Academician Dubinin referred to the completion of extensive investigations on the radiochemistry of the products of nuclear reactions occurring the bombardment of uranium, thorium, bismuth, and copper with high-energy particles. A study was made of the yields of fission products and the positions of the elements in the periodic system, the identities of the particles formed by radioactive decay, and the energies of these particles. New b-active isotopes were discovered, and some new a-radiators were found among the rare earths. The progress of work on the geochemistry of isotopes has enabled estimates to be made of the age of Ukrainian precambrian rocks by a comparative method based on determinations of uranium-lead, strontium-rubidium, and argon-potassium ratios. Investigations on the geochemistry of lead enabled several questions concerning the ore-formation process to be resolved.

Investigations of great importance were carried out on the chemistry of the rare elements. For example, a complete scheme for the separation and isolation of all fifteen rare-earth elements was worked out experimentally. Work on the separation of zirconium and hafnium was completed and brought into practical application. Spectrum, x-ray spectrum, and radioactivity methods were developed for the determination of extremely small amounts of rare elements in pure niobium, tantalum, zirconium, tungsten, molybdenum, and other metals. The x-ray-spectrum investigations were completed by the development of a theory of the fine structure of solids.

The report referred also to work of the institute on biogeochemistry. This established the causes of deleterious effects on animals and plants in some districts of the country due to insufficiency or excess of copper, molybdenum, lead, strontium, cobalt, and other elements.

As Academician Dubinin stated, the activities of the Institute of Silicate Chemistry have developed in various directions: heterogeneous equilibria and phase transformations in silicate systems had been studied, and work had been carried out on the hydrothermal synthesis of calcium hydrosilicates and on the study of hydrogen bonding in these by the method of infrared spectroscopy. The polymorphous transformations of silica were studied by methods of adiabatic calorimetry and thermography. Investigations were carried out for industry on organosilicon coatings, on ceramics, on the introduction into industry of new progressive technology in the polishing of glass, and on other subjects.

In its connection with hydroconstruction, the work of the Hydrochemical Institute is of great importance for the national economy. Academician Dubinin referred to the study of the hydrochemical regime in the Volga immediately before the flooding of the Kuibyshev and Gorky reservoirs, the prognosis of the mineralization and change in chemical composition of the waters of Lake Balkhash that would result from the projected hydrotechnical construction in that region, and other laboratory and field work of the institute.

The Institute of Physical Chemistry is notable for the great variety of the work which it carries out. In his report, M. M. Dubinin referred to some of the most important of these lines of work. In the field of electrochemistry and chemical sources of current, a new method was developed for the investigation of the mechanism of the separation of molecular hydrogen in the electrolysis process, and it was shown for the first time that atomic hydrogen has an oxidizing function and passes into molecular hydrogen at the electrode at high overvoltages as a result of simultaneous combination with a hydrogen ion and an electron. With the aid of labeled atoms, new data were obtained concerning the mechanism of the electrodeposition of chromium. By the same method, the transfer of silver and antimony from the lattice of the positive plate of an accumulator to the negative plate was studied. The effect of organic substances on the self-discharge of a zinc electrode was studied. Among investigations on the corrosion of metals, the speaker referred to work on the principles underlying a new method for the electrochemical protection of stainless steels by means of anodic polarization, to investigations on the mechanism of the corrosion of metals in soils (which showed the dependence of the rate of corrosion on the salinity and moistness of the soils), and to various other investigations.

In the same institute, said M. M. Dubinin, 1955 saw the completion of work on the mechanism of the effect of an active medium on creep and fatigue in metals and its publication as a monograph. A physicochemical investigation was carried out also into the fine vibrational grinding of cements, and this has provided a basis for a new technology of building materials. In connection with the study of aerosols, a convenient continous method has been devised for measuring critical supersaturations at condensation nuclei, and a simple continuous counter has been designed for these nuclei.

In the catalysis field, several investigations have been completed on the electronic theory of catalysis on semiconductors, the modifying effect of nonmetals in the catalytic preparation of ethylene oxide has been confirmed, and it has been shown that the selectivity and activity of catalysts can be raised. The classification of catalytic processes according to the nature of the primary act has been improved, and a theory for the selection of catalysts of the acid-base type has been developed.

In 1955 the work of the Institute of Chemical Physics was centered on the kinetics and mechanisms of chemical reactions. The concept of macroscopic stages in chemical processes and the special part played by the initial period was developed and provided with experimental support. The results of this work give reason to suppose that the solution of the problem of directing a chemical process is associated with action directed onto the macroscopic stages.

Experimental investigation has established the main features of mechanism of the action of aprotonic acids in acid-catalyzed reactions. It was shown for the first time that aprotonic acids of the boron trifluoride type act like protonic acids: they form complexes with various substances, and the products are powerful protonic acids.

Academician Dubinin then passed to work on organic chemistry and discussed the investigations carried out at the Institute of Heteroorganic Compounds. In this institute, work has continued on the chemistry of organometallic compounds, and of ferrocene in particular. A large number of ferrocene derivatives have been prepared, and the effect of substituents on the activity of the cyclopentadiene rings of the ferrocene molecule has been determined. In the organophosphorus field, the theory of tautomerism has been examined in the light of the tautomeric equilibrium of lactim-lactams, dialkyl hydrogen phosphorothioates, etc. Many compounds having insecticidal action have been synthesized. In the organosilicon field, a beginning has been made in the development of methods of synthesizing organic polymers containing a chain of silicon and aluminum atoms linked through oxygen atoms.

An extensive investigation of the telomerization of ethylene with carbon tetrachloride and with chloroform has enabled the conditions to be found under which the higher tetrachloroalkanes (odd members of the series containing up to 51 carbon atoms in the molecule) could be prepared at a comparatively low pressure. For the first time, the effect of pressure and of the relative amounts of the reactants on the yield of practically important telomerization products has been determined. Methods for the synthesis of various carboxylic acids, amino acids, amino alcohols, etc. have been devised.

In the field of macromolecular compounds, a number of theoretical problems on the effect of the structures of the original reactants on the properties of the resulting polymers have been solved. Many new polymers have been synthesized from various dicarboxylic acids and various bifunctional compounds. These include polymers containing silicon, sulfur, and phosphorus. The properties of the polymers obtained have been studied.

Referring to the work of the N. D. Zelinsky Institute of Organic Chemistry, the speaker pointed out the substantial progress in investigations associated with the development of the theory of chemical structure and the extension of theoretical and experimental investigations on heterogeneous catalysis. New regularities have been discovered in the structural and spatial directivity of the diene synthesis. Hydration, cyclization, isomerization, and oxidation reactions have been studied, and their mechanisms have been established with the aid of labeled atoms. Methods have been developed for the building up of carbon chains of the isoprenoid type from acetylenic alcohols. These make it possible to effect the complete synthesis of some important natural substances. Work has been completed on the development of new methods of synthesis of the new sedative isopromedol and on the clinical testing of this substance.

The multiplet theory of catalysis has been developed further, particularly the aspects of energetic correspondence and quasiheterogeneous surfaces. With the aid of the kinetic method, an extensive investigation has been made in order to determine the bonding energy between the reacting molecules and the catalyst. For the first time in heterogeneous catalysis it has been proved experimentally that the hydrocondensation of carbon monoxide with olefins proceeds by a chain mechanism.

The work of the Institute of Macromolecular Compounds has centered mainly around the problem of establishing the relationship of the chemical structures of the reactants and the polymerization conditions to the structure and properties of the polymers. A theory has been advanced which provides a semiquantitative explanation of the phenomena occurring when high polymers pass into the vitreous state and when they are annealed. The theory has enabled a relationship to be established between the vitrification temperature and the characteristics of the substance. New data have been obtained concerning the activity of the double bonds

of vinyl compounds in reactions with free radicals. Investigations on ion exchange have been completed, and principles that can form the basis of a theory of chromatography and the exchange of large ions have been laid down.

Investigations of vinyl compounds have enabled new transparent polymeric compositions to be developed and the future course of work on such polymers to be planned. Work on the synthesis of macromolecular compounds having new or specific properties has resulted in the development of polymers which are now to be produced on a larger scale in conjunction with industrial organizations.

After his review of the activities of the institutes of the Division of Chemical Sciences, Academician Dubinin reported that in 1955 there were seven sessions of the Division at which one general progress report and thirty-two scientific papers were read and discussed. Work on the July Session on the Peaceful Uses of Atomic Energy, the preparation of reports for the Geneva conference, and the organization of the chemical section of the Exhibition on the Peaceful Uses of Atomic Energy all occupied important places among the activities of the Division.

The speaker referred to the considerable changes that had occurred in the publishing activities of the Division. Three new journals had been brought into being: The Journal of Inorganic Chemistry, The Journal of Scientific and Applied Photography and Cinematography, and Geochemistry. Moreover, the sizes of several other journals had been increased.

Academician M. M. Dubinin noted with satisfaction the considerable strengthening of scientific ties with foreign scientists. An agreement had been reached with the chemical societies of Britain and France concerning the exchange of scientific papers for publication in the journals of each country. This form of close collaboration and mutual exchange of information, stated the speaker, will a find a wide basis for development in the future, both here and abroad.

There were more than twenty participants in the discussion on M. M. Dubinin's report.

Academician S. I. Volfkovich drew attention to the need for the publication of more books on methods more encyclopedias, and more reference books; these must be written by suitable teams of authors. S. Z. Roginsky, Corr. Member Acad. Sci. USSR, expressed the opinion that it is essential to proceed vigorously in the further extension of the material basis of work on the problem of catalysis. Academician Rebinder pointed out the importance of rapid publication of comments on completed scientific investigations of theoretical importance or of importance to the national economy. S. N. Danilov, Corr. Member Acad. Sci. USSR, referred to the necessity of extending the laboratories of the Division and equipping them fully.

N. A. Bakh, Doctor Chem. Sci., discussed the desirability of re-examining the system of training scientific staffs with the object of ensuring that the institutes will be better provided with creative workers. I. P. Alimarin, Corr. Member Acad. Sci. USSR, pointed out the importance of the better coordination of scientific investigations; he referred, in particular, to the field of analytical chemistry. Moreover, better technical equipment with modern apparatus was necessary, particularly for the outlying scientific establishments. Academician I. L. Knunyants made an appeal for the intensification of scientific investigation into the chemistry of proteins. He made some remarks on individual papers on proteins that have been published in recent years, and he discussed also some problems of scientific organization. Academician A. N. Frumkin criticized the work of the Journal of Physical Chemistry and pointed out the necessity of strengthening international relations, particularly with respect to the problem of electrochemical kinetics. Ya. K. Syrkin, Corr. Member Acad. Sci. USSR, referred to the inadequate development of investigations on the theory of chemical structure, and he emphasized the significance of the investigations of the Kazan scientists Zavoisky and Kozyrev on paramagnetic resonance.

I. M. Lepeshkov, Doctor Chem. Sci., emphasized the importance of developing investigations on inorganic chemistry and the necessity of extending the material basis for these investigations. Academician V. A. Kargin pointed out the importance of research leading to the development of new directions in chemical science. Academician A. P. Vinogradov drew attention to the useful purpose that would be served by a new publication or new sections in existing journals having the object of systematically acquainting workers in particular branches of science with the investigations of others in that field. In A. P. Vinogradov's opinion, this procedure would provide the best means of effecting the satisfactory coordination of scientific investigations.

On questions relating to the organization of scientific work, contributions to the discussion were made by M. I. Nikitin, Corr. Member Acad. Sci. USSR; Academician N. N. Semenov; O. A. Alekin, Corr. Member Acad. Sci. USSR; V. M. Vdovenko, Doctor Chem. Sci.; N. A. Toropov, Doctor Chem. Sci.; N. I. Shulkin, Corr. Member Acad. Sci. USSR, and others.

In some concluding remarks, Academician M. M. Dubinin referred to some criticisms sent to the Bureau of the Division; these criticisms were justified and were of importance, and he suggested that members of the Bureau should study them carefully and take them into account in their further work.

At the final session of the Annual Meeting of the Division of Chemical Sciences, the participants listened with interest to a paper by Academician V. N. Kondratyev on "Lines of Progress in the Theory of the Chemical Process".

The paper was followed by a discussion.

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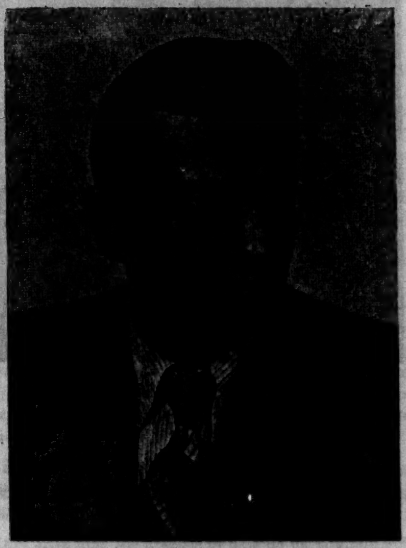


IVAN LYUDVIGOVICH KNUNYANTS

Dear Ivan Lyudvigovich:

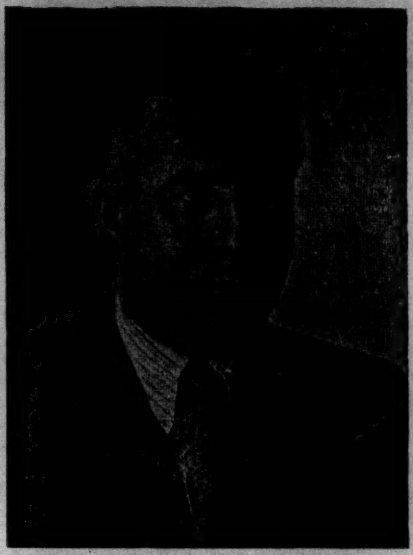
The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, warmly congratulate you on the attainment of the age of fifty.

It is with great satisfaction that we note your varied scientific activities in the chemistry of heterocyclic and natural substances, macromolecular compounds, and fluorine.

May you make further creative progress in your scientific work.

Division of Chemical Sciences,
Academy of Sciences of the USSR

Editorial Board of the Bulletin of the Academy of
Sciences of the USSR, Division of Chemical Sciences



IVAN NIKOLAEVICH NAZAROV

Dear Ivan Nikolaevich:

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, warmly greet and congratulate you on the occasion of your fiftieth birthday.

Your fruitful scientific activity over many years in many fields of organic chemistry is well known to chemists everywhere.

Accept our best wishes for your health and further success in your creative work in the service of our Fatherland.

Division of Chemical Sciences,
Academy of Sciences of the USSR

Editorial Board of the Bulletin of the Academy of
Sciences of the USSR, Division of Chemical Sciences

COLLOIDAL PROPERTIES OF POLONIUM •

I. E. Starik, N. I. Alekseenko, and N. G. Rozovskaya

The question of the state in which extremely minute amounts of a substance are present in a solution is a fundamental and highly controversial problem in radiochemistry. For various reasons, great experimental difficulties were met in the solution of this problem, and as a result there are now two directly opposed points of view on the matter. According to one of these, radioactive elements in microconcentrations are able to form colloidal solutions, in spite of the fact that the solubility product is not attained. The possibility of the formation of colloidal solutions is associated by some authors with specific properties of the radioactive elements [1]. According to the second point of view, the radioactive elements are present in the ionic state under these conditions, but they are absorbed by colloids present in the solution and therefore behave like colloids [2].

There are three main causes for the difficulty met in the solution of this problem.

1. No methods exist which will unequivocally resolve the question of the nature of radiocolloids. It is not a matter of increasing the sensitivity of existing methods of colloid chemistry, but of the difficulty in principle of finding a method that would give an answer to the question. Actually, workers on this problem, from Paneth onward, used all of the existing methods in order to determine whether the radio-elements investigated were colloidal, and it appeared that, in view of the proofs they obtained by many methods of the colloidal nature of these elements, there could be no doubt about the solution of the problem. However, as Zsigmondy correctly pointed out, a study of the colloidal behavior of these elements by the usual methods does not enable us to decide whether they themselves are true colloids, or whether they are adsorbed by extraneous colloids that are always present in solutions.

2. It is wrong to pose this question of the colloidal nature of radio-elements in solutions in its general form, for such a question must depend for its solution on the chemical nature of the elements and on the conditions under which they are studied.

3. Substantial difficulties arise from the absence of data on the solubilities of compounds of the radio-elements investigated and from the complications met in the determination of such solubilities, for at such low

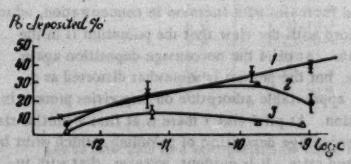


Fig. 1. Relation of deposition of polonium on copper to the concentration of polonium at pH: 1) 1; 2) 4; 3) 13.

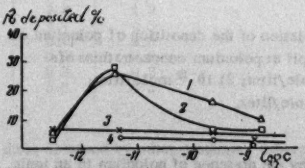


Fig. 2. Relation of deposition of polonium on copper to the concentration of polonium at pH: 1) 6; 2) 7; 3) 8; 4) 9.

• Paper read at a general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR on October 27, 1955.

concentrations adsorption and other processes make this determination very difficult. Moreover, the results of solubility determinations depend greatly on the assumption made regarding the degree of hydrolysis or ionization.

In the period of more than forty years that has elapsed since the investigations of Paneth [3] and Godlewski [4], many attempts have been made to solve this problem and to extend these investigations to all artificial radio-elements, but even now the question of the existence of radio-elements as true colloids still remains a controversial one. We shall not discuss the history of this problem, but it may be noted that a large number of investigators took part in these investigations [3-14]. It must be emphasized that the most important investigations were those of Paneth, Hahn, Haissensky, and Chamie.

It appeared to us that the solution of the question of principle involved in this problem – the possibility of the existence of true colloids in very dilute solutions – could be most conveniently attempted for the case of polonium, although work with this element is made very difficult by the existence of a large number of valency states, the complexities met in the determination of these, and the amphoteric character of the element. As one of us has shown previously [15], this question can be solved by the application of only one method – the indirect method of adsorption. It was shown that adsorption of polonium by negatively charged surfaces – such as glass, and also colloids – is at a minimum in neutral and weakly alkaline media, i.e. in those media in which its colloidal properties are at a maximum. If polonium exhibits colloidal properties because it is adsorbed on extraneous colloidal particles, then it would be expected that its colloidal properties would be most marked in an acid medium, and not in the neutral and alkaline media in which it is actually observed.

The proposed method appears to give an unequivocal answer to the question, but some investigators still do not reject the adsorption theory of the nature of radiocolloids. We therefore considered it necessary to use several methods, the results of which, taken together, would provide a more unequivocal solution of the question and would give a clearer picture of the state of polonium in various media. We used the following methods: 1) electrochemical deposition on metals; 2) adsorption and desorption of polonium at a glass surface; 3) centrifugation; 4) ultrafiltration; 5) radiography. With the object of resolving the question of the polydispersity of polonium solutions, each polonium solution was investigated three times by each of these methods.

Let us pass now to an examination of the results of the study of the electrochemical deposition of polonium on copper in solutions varying in pH and concentration. It may be expected that appreciable deposition of polonium on copper will occur in those media in which the polonium is mainly in the ionic state; in those media in which the polonium is hydrolyzed and forms colloidal solutions, the effective concentration of polonium ions will be much less and the amount of polonium deposited on copper should also be appreciably less. The following conclusions can be made from an examination of the curves in Figures 1 and 2. For each value of the pH, the relation between the amount of polonium deposited and its concentration in the solution has its own characteristic features. At pH 1 we find that the percentage of the polonium deposited increases with increase in concentration, which is in accord with the view that the polonium is in the ionic state. At pH 4 the percentage deposition again increases, but the process is somewhat distorted as a result of appreciable adsorption on impurities present in the solution. At pH 6 and 7 there is at first a similar rise in the percentage deposition of polonium, which must be explained by the presence of polonium in an ionic, nonhydrolyzed state. It is evident, however, that with increase in the polonium concentration hydrolysis begins to have an effect, which becomes greater at pH 7.2, since the sharper fall in the percentage deposition of polonium occurs at this pH. Above a concentration of $1.77 \cdot 10^{-10}$ mole/liter, the percentage deposition of polonium at pH 7.2 remains constant. At pH 8 and 9 the percentage deposition of polonium on copper is independent of the polonium concentration and is represented by a straight line (Fig. 2).

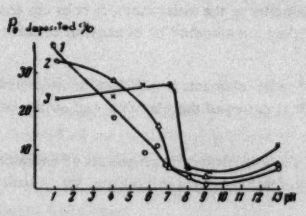


Fig. 3. Relation of the deposition of polonium on copper to pH at polonium concentrations of: 1) 10^{-9} mole/liter; 2) 10^{-10} mole/liter; 3) 10^{-12} mole/liter.

It is natural to suppose that, in these media at all of the concentrations investigated, polonium forms insoluble compounds. Confirmation of the presence of insoluble compounds in these media is provided by the

fact that the percentage of the polonium separated is identical in three successive depositions from the same solution (Table 1). Actually, if in the first deposition of polonium on copper a definite though very small amount of polonium ions is deposited and in the course of the day that passes between two successive depositions the ions are replaced by partial dissolution of the solid phase and reestablishment of equilibrium, then the effective concentration of ions will attain its previous value.

It is of interest to note also that, as can be seen from Fig. 3, the pH at which the sharp reduction in the deposition of polonium occurs depends on its concentration:

Conc. Po	pH	$L_{Po(OH)_4}$
$5{,}2\cdot10^{-12}$	7,6	$1{,}3\cdot10^{-57}$
$1{,}8\cdot10^{-10}$	7,2	$6{,}8\cdot10^{-58}$
$1{,}7\cdot10^{-9}$	6,9	$7{,}1\cdot10^{-58}$

On the basis of these results an idea can be obtained of the solubility of the hydrolysis products and the solubility product of the postulated hydrolysis product can be estimated. Hence, a study of electrochemical deposition enables us to characterize the various states of polonium in various media.

TABLE 1

Deposition of Polonium on Copper

pH	Concentration of polonium in the solution (mole/liter)	Polonium deposited (%)		
		First deposition	Second deposition	Third deposition
1.2	$5.22\cdot10^{-12}$	23	24	18
4.2	$5.22\cdot10^{-12}$	23	7.3	2.9
5.8	$3.82\cdot10^{-12}$	26.5	10.0	8.4
7.2	$3.82\cdot10^{-12}$	27	15.7	8.9
8.0	$5.22\cdot10^{-12}$	5.3	5.6	4.6
9.3	$5.22\cdot10^{-12}$	3.9	5.0	10.0
13	$5.22\cdot10^{-12}$	10,7	4.8	4.1
1.2	$1.49\cdot10^{-10}$	33	35	51
4.2	$1.77\cdot10^{-10}$	28	6.1	2.9
6.6	$1.40\cdot10^{-10}$	16	8.0	5.1
7.1	$1.77\cdot10^{-10}$	5.3	7.2	5.7
8.0	$1.77\cdot10^{-10}$	5.1	2.8	3.4
9.0	$1.77\cdot10^{-10}$	3.0	2.0	3.1
13	$1.77\cdot10^{-10}$	6,0	6.5	4.8
1.1	$1.09\cdot10^{-9}$	37	40	54
4.2	$1.18\cdot10^{-9}$	17	6.6	3.6
5.8	$1.73\cdot10^{-9}$	9.1	2.8	1.9
6.6	$1.09\cdot10^{-9}$	11,0	4.7	4.5
6.9	$1.73\cdot10^{-9}$	6.0	5.2	2.3
8.1	$1.18\cdot10^{-9}$	2.4	0.6	0.8
9.1	$1.18\cdot10^{-9}$	0.5	0.3	0.2
13	$0.77\cdot10^{-9}$	5.0	5.0	8.2

Let us now pass to a comparison of these results with those obtained by other methods. Adsorption experiments were carried out with glasses of various compositions, including quartz glass. It must be pointed out that the limits of reproducibility in these experiments were about 15%. The adsorption of polonium on different kinds of glass (Table 2) followed a different course in each separate case, but it was established quite firmly that in all cases adsorption was at a minimum in a neutral medium.

Special attention was paid to a more detailed study of the relation between adsorption on one kind of glass and the concentration of polonium in the original solution. It is quite obvious that, if polonium forms true colloids subject to the mass-action law, then this factor is very important. As can be seen from Fig. 4, at a polonium concentration of 10^{-10} mole/liter, the adsorption maximum lies in the pH range 4.2-6 and the minimum in the range 8-9.

The explanation of the existence of a maximum may be that with rise in pH from 1 to 4 the hydrogen ion concentration falls and creates favorable conditions for considerable adsorption of polonium ions. However, with further rise in pH the degree of adsorption falls, probably as a result of the occurrence of hydrolysis of polonium compounds. It is interesting that at pH 7.2 the degree of adsorption is fairly high, even when the polonium concentration is 10^{-10} mole/liter, a concentration at which – as we have seen from the electrochemical experiments – insoluble compounds are formed. The probable explanation is that in this medium colloidal polonium particles are still positively charged and are therefore adsorbed to a fair extent by the negatively charged glass. At a pH of about 8, however, the charge of the colloidal particles changes in sign, so that adsorption by the glass stops. At pH 8-9 adsorption is at a minimum, which may be explained by the formation of insoluble compounds and a considerable reduction of the ionic component.

The existence of an equilibrium between the soluble and insoluble parts is indicated by the absence of any difference in the degree of adsorption in repeated operations at pH 8-9 (Table 3). It is true that the degree of adsorption varies little in three successive experiments at pH 1, but in this case there is no reason to doubt

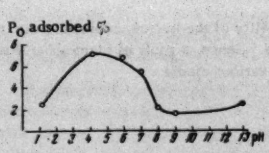


Fig. 4. Dependence of the adsorption of polonium on glass on pH at a polonium concentration of 10^{-10} mole/liter.

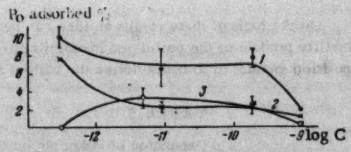


Fig. 5. Dependence of the adsorption of polonium on glass on the polonium concentration at pH: 1) 4; 2) 1; 3) 13.

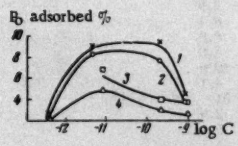


Fig. 6. Dependence of the adsorption of polonium on glass on the polonium concentration at pH: 1) 6; 2) 7; 3) 8; 4) 9.

that the polonium is in the ionic state and, moreover, at such low pH its tendency to be adsorbed is low so that the concentration of the solution after the adsorption experiment is very little different from the concentration after a day has elapsed; each successive adsorption, therefore, is carried out under almost identical conditions, and the degree of adsorption will remain constant. At all other values of pH the extent of the second adsorption is less, probably as a result of the adsorption of polonium ions on impurities present in the solution and the competition between the two adsorption processes. At a concentration of the order of $8 \cdot 10^{-10}$ mole/liter, the degree of adsorption is considerably lower than at lower polonium concentrations, but the absolute amounts of adsorbed polonium at concentrations of $1.8 \cdot 10^{-10}$ and $8 \cdot 10^{-10}$ mole/liter are almost identical. These results indicate that adsorption of polonium on the glass surface is nearing its saturation point. The amount of adsorbed polonium is $5 \cdot 10^{-14}$ g-atom/sq. cm.

Let us now examine the relation of the adsorption of polonium at various values of pH to the polonium concentration (Figures 5 and 6). In the pH range 1-4 polonium is mainly in the ionic, nonhydrolyzed state, and the degree of adsorption falls with rise in the polonium concentration, thus indicating the gradual saturation of the surface of the adsorbent. In the region of pH 6 and 7 polonium is probably in the hydrolyzed state to an appreciable extent, and at first the degree of adsorption increases with increase in the polonium concentration; it quickly attains saturation, however, and it then falls. In the pH range 8-13 the degree of adsorption is low and changes very little with change in the polonium concentration. The general character of the variation of the adsorption is similar to that represented by the curves for pH 6 and 7, although the degree of adsorption is considerably less in the pH range 8-13. In this respect the curves are very similar to those for the electrochemical deposition of polonium on copper and indicate the existence of an ionic component in equilibrium

TABLE 2

Degree of Adsorption (%) of Polonium by Glasses Differing in Composition

Medium / Kind of glass	0.1*N* HNO_3	0.01*N* HNO_3	Neutral	0.001*N* NaOH	0.1*N* NaOH
Quartz glass	2.7	—	0.2	—	0.6
L-36	1.3	2.4	0.6	1.6	2.8
No. 23	1.1	1.7	0.4	0.8	0.9
L-100	0.8	1.8	0.3	—	—
31-4	0.7	1.4	0.6	1.3	1.2

with insoluble polonium compounds. We see, therefore, that the results on the adsorption of polonium by glass are in full agreement with the results on the electrochemical deposition of polonium on copper.

The results obtained on the desorption of polonium from glasses of various compositions completely confirm the views derived from the study of adsorption with respect to the state of the polonium in the different media. By way of example we give curves for the desorption of polonium by means of 1 N HNO_3 from L-36

TABLE 3

Adsorption of Polonium by Glass

pH	Concentration of polonium in the solution (mole/liter)	Degree of adsorption (%)		
		First experiment	Second experiment	Third experiment
1.2	$8.29 \cdot 10^{-12}$	2.2	1.8	1.3
4.2	$8.29 \cdot 10^{-12}$	6.6	2.9	3.2
5.8	$8.29 \cdot 10^{-12}$	7.0	1.0	0.8
7.2	$5.22 \cdot 10^{-12}$	6.2	2.7	1.9
8.0	$5.22 \cdot 10^{-12}$	4.9	3.1	2.4
9.3	$5.22 \cdot 10^{-12}$	2.8	2.6	2.2
13	$5.22 \cdot 10^{-12}$	3.3	1.5	1.4
1.2	$1.8 \cdot 10^{-10}$	2.6	1.0	1.1
4.2	$1.8 \cdot 10^{-10}$	7.6	7.2	4.1
6.0	$1.8 \cdot 10^{-10}$	7.2	2.3	1.1
7.2	$1.8 \cdot 10^{-10}$	5.5	3.4	2.0
8.0	$1.77\ 10^{-10}$	1.8	2.1	1.7
9.0	$1.77 \cdot 10^{-10}$	0.9	0.5	0.4
13	$1.77 \cdot 10^{-10}$	2.5	2.5	1.4
1.1	$7.73 \cdot 10^{-10}$	1.1	0.9	0.9
4.2	$7.73 \cdot 10^{-10}$	1.9	2.7	2.3
6.1	$7.73 \cdot 10^{-10}$	2.2	2.6	2.6
7.1	$7.73 \cdot 10^{-10}$	1.6	1.5	1.5
8.1	$8.85 \cdot 10^{-10}$	1.6	0.6	0.6
9.1	$8.85 \cdot 10^{-10}$	0.5	0.6	0.5
13	$8.85 \cdot 10^{-10}$	0.3	0.2	0.2

(Pyrex type) glass and from quartz glass (Figures 7 and 8). The preliminary adsorption was from solutions of polonium in water and in 0.1 N HNO_3. Degree of desorption (%) is plotted as ordinate and time (hours) as abscissa. The results show that there is a great difference in the desorbing effect of 1 N HNO_3 according as the adsorption of the polonium is from distilled water or from 0.1 N HNO_3; this is most readily explained by a difference in the state of the polonium. According to our views, in distilled water polonium is mainly in the colloidal form and in 0.1 N HNO_3 it is mainly in the ionic form, so that it may be expected that a difference

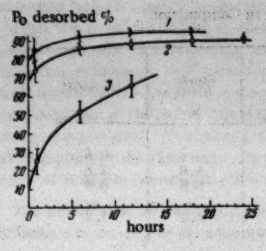


Fig. 7. Dependence of the desorption of polonium from glass L-36 by means of 1 N HNO_3 on the conditions of adsorption:
1) from water; 2) from 0.1 N NaOH; 3) from 0.1 N HNO_3.

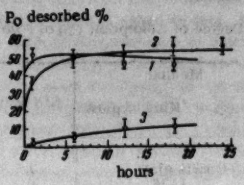


Fig. 8. Dependence of the desorption of polonium from quartz glass by means of 1 N HNO_3 on the conditions of adsorption:
1) from water; 2) from 0.1 N NaOH; 3) from 0.1 N HNO_3.

will be found in the desorption, colloidal particles being less firmly bound to the sorbent surface than multivalent cations are. The experiments confirmed this view. Also, the difference in the character of the desorption kinetics in these two cases should be noted: this again supports the views that we have expressed. The difference in character between the curves for the desorption of polonium adsorbed from water and from 0.1 N HNO_3 may be associated also with the diffusion of polonium ions into glass from a medium of 0.1 N HNO_3.

The results we obtained on centrifugation and ultrafiltration again confirmed the above-stated views on the state of polonium in various media. The centrifugation results provide a criterion of the degree of dispersity of the particles. The use of our usual centrifuges permits the precipitation of particles of about 10 μ in radius, i.e. the fraction of the polonium which is associated with coarsely dispersed particles is centrifuged out. In centrifugation experiments adsorption occurs on impurities present in the solution and on the walls of the centrifuge tubes, so that the results are of poor reproducibility and are semiquantitative in character. The results showed that the centrifugation affected only coarsely dispersed particles carrying adsorbed radio-element, for the centrifugation maximum corresponds to the adsorption maximum for polonium (Fig. 9); in those media in which polonium exhibits mainly colloidal properties, the amount of polonium centrifuged out – as also the degree of adsorption – tends to zero. The centrifugation results confirm that at pH 8-10 polonium forms mainly insoluble compounds.

The ultrafiltration results, like the centrifugation results, provide a criterion of the dispersity of the particles. In our preliminary experiments we used industrial ultrafilters having a mean pore diameter of 300 mμ, so that they could retain only coarsely dispersed particles. The results obtained by the ultrafiltration method showed (Fig. 10) that in this case the maximum retention of polonium by the ultrafilters coincided with the maximum tendency for polonium to be adsorbed. The retention of polonium was at a minimum in those media in which polonium is present in the colloidal form. The ultrafiltration experiments, therefore, are in full accord with the results obtained by other methods.

In conclusion, we shall discuss briefly the radiographic method, which finds extensive application in the study of the state of radio-elements in solution. The radiographic method was first applied to solutions by Chamie [16] in 1927. The method consists essentially in the application of a drop of the solution of radio-elements either directly to the surface of a photographic plate, or to a piece of mica placed in contact with the photographic emulsion, or to vaseline smeared on the plate to protect it from the chemical action of the solution. Chamie's photographs indicated a nonhomogeneous distribution of activity and the presence of groups of atoms. The author calculated that each such group contained 10^6-10^8 polonium atoms, so that such a group could not consist only of polonium atoms and must be an adsorption complex. In Chamie's opinion, such groups exist in the solution itself and are not formed when the solution comes into contact with the surface. The results of further investigations by the radiographic method – by Herzfinkel and Jedrzejowski [11], Hahn [8], Werner [7], and Blau and Rona [12] – confirmed Chamie's views and lent them precision.

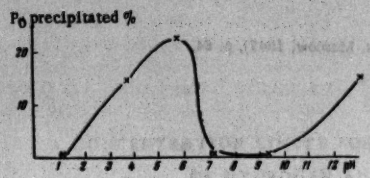


Fig. 9. Relation between the precipitation of polonium by the centrifugation method and the pH for a polonium concentration of 10^{-12} mole/liter.

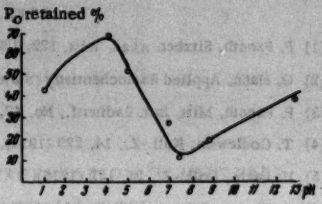


Fig. 10. The ultrafiltration of polonium from solutions of various pH at a polonium concentration of 10^{-9} mole/liter.

Radiography as applied to solutions is generally regarded as a method of studying what is happening in the solution, and the possible adsorption of radio-elements by the mica, vaseline, paraffin, or photographic emulsion to which the solutions of the radio-elements are applied is not taken into account.

Shortly after the appearance of Chamie's first papers, one of us, in collaboration with Diezenrot-Mysovskaya [17], showed experimentally that it is the polonium adsorbed on the mica applied to the photographic plate that is effective in the radiography, the image formed being characteristic only of the adsorption of polonium by mica. In the present investigation we made a detailed study of the distribution of polonium in photographic emulsions impregnated with polonium solutions differing in concentration and pH, and we compared this distribution with that of polonium on a mica or glass surface. We found that, in all cases, the distribution of polonium was similar in character: the radiographs showed a nonhomogeneous distribution of activity and the presence of aggregates of active atoms. A quantitative investigation of the absorption of polonium by the photographic emulsion as a function of pH and a comparison of this process with the adsorption of polonium on mica and on glass under similar conditions showed that the processes were undoubtedly similar and were similarly affected by pH changes. These results enable us to assert that radiographs obtained in these ways give us a picture only of the adsorption of the radio-element at the surface in contact with the solution, the aggregates of active atoms observed on the radiographs being adsorptional formations. The radiographic method, therefore, is applicable to the study of the state of radio-elements in solution only as a method for the study of adsorption in general. Thus, radiography gives results in accord with other methods, but permits us to study only adsorption phenomena at the surface of contact with the solution, and not the state of the radio-elements in the solution itself.

We consider that the results obtained by the use of various methods of investigation — 1) adsorption by glass, 2) desorption from glass, 3) electrochemical deposition on copper, 4) centrifugation, 5) ultrafiltration, 6) the use of all of the methods at various polonium concentrations, 7) the performance of three successive experiments on a given solution, 8) radiography — enables us not only to give an unequivocal answer to the question of the existence of polonium in the true colloidal state, but also to define more precisely the conditions under which polonium occurs in the various conditions.

The study of the electrochemical deposition of polonium enabled us to calculate approximate values of the solubilities of polonium compounds. These values, of course, are not very accurate, but they undoubtedly give an idea of their order of magnitude and enable us to explain the formation of colloids of the radio-elements on the basis of our usual concepts. In the formation of radio-colloids, therefore, there is nothing specific that must be associated with their radioactive nature, and all the results obtained can be applied to the usual elements.

We are applying these methods also to other elements: uranium, ruthenium, radium, etc. We consider that the systematic study that we have now begun with the aid of these methods with the object of determining the behavior of radio-elements in the low-concentration range will enable us to obtain more accurate knowledge of the properties and peculiarities in behavior of micro-quantities of these elements.

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CONCENTRATION LIMITS FOR FLAME PROPAGATION IN MIXTURES OF HYDROGEN AND OXIDES OF NITROGEN

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It has been long known that hydrogen is able to form explosive mixtures not only with molecular oxygen, but also with chemical compounds containing oxygen in the bound state. The system of this kind that is most frequently encountered is H_2–N_2O [1, 2, 3]. There are some investigations also on the explosive character of H_2–NO mixtures [4, 5, 6]. There are no data in the literature on the explosion of H_2–NO_2 mixtures; the displacement of the ignition field due to additions of NO_2 to hydrogen-air mixtures at low pressures has been determined [7], and rates of flame propagation and flame temperatures were recently determined for mixtures of hydrogen with NO and NO_2 [8].

The paper [1] gives data on the limits of flame propagation in mixtures of hydrogen and nitrous oxide spark-ignited in closed steel tubes 1.6 cm in diameter. Under these conditions, flame is propagated in mixtures containing not less than 5% of hydrogen (lower limit) and not more than 75% of hydrogen (upper limit). Data are given also on the narrowing of the flame-propagation field in presence of nitrogen, argon, helium, and carbon dioxide. The inhibiting effect of these additives on flame propagation in H_2–N_2O mixtures diminshes along the series He > CO_2 > N_2 > Ar. In a later investigation [2], a more accurate value was obtained for the upper limit for flame propagation in H_2 + N_2O mixtures, but the value of 83.9% given by these authors is nevertheless somewhat less than the value obtained in the present investigation. In the investigation [3] on the limits for flame propagation in hydrogen-air mixtures, the displacement of the limits when oxygen was replaced by nitrous oxide was also determined. There was some change in the lower limit, and the upper limit was lowered to a greater extent than would be expected from the amounts of oxygen in N_2O and O_2 molecules.

Although it has been known since, at the latest, 1887 [5] that hydrogen forms explosive mixtures with nitric oxide, the concentration limits for flame propagation in such mixtures were determined much later [6] (lower limit 13.5% H_2; upper limit 49.4% H_2). When the H_2–NO mixture was diluted with 10% on its volume of nitrogen, the limits for flame propagation were narrowed (lower limit 14.3%; upper limit 37.0%). These experiments were carried out in an explosion buret, diameter 1.5 cm and length 30 cm, provided with a platinum spark gap for the ignition of the mixture (the power of the spark is not given in the paper).

As will be seen from this short review, the papers cited contain mainly fragmental information on the explosive character of mixtures of hydrogen with N_2O and NO. The concentration limits given in these papers are generally low in comparison with those observed in our investigations. This fact is probably associated with the use by these authors of explosion vessels of small diameter and of insufficiently powerful sources for the ignition of the flammable mixture. Moreover, the study devoted to the effect of inert diluents on the flame-propagation field is quite inadequate. It was of interest to obtain complete information in a single investigation on the flame-propagation fields in mixtures of hydrogen with oxides of nitrogen and inert diluents.

EXPERIMENTAL

Experimental Procedure

As is well known, the values of the concentration limits for flame propagation depend on the dimensions of the vessel, the powerfulness of the ignition source, the temperature and pressure of the mixture, the presence of various additives in the mixture, the conditions of mixing the mixture, the ability of the mixture to propagate a cool flame, etc. The experimental procedure must be selected, therefore, with due regard to the effects of these factors.

The concentration limits are widened as we pass from narrow tubes to wider ones, but it is known that for vessels of diameter greater than 5 cm the dimensions cease to have any effect on the values of the limits. In the present investigation we used explosion flasks 8 cm in diameter, so that the effect of this factor on the values of the limits was excluded. With rise in temperature the concentration limits are widened. Increase in pressure greatly raises the upper limit, but has only a small effect on the lower limit. Reduction of the pressure to below atmospheric results in a closer approach of the upper and lower limits for flame propagation. In our investigation we did not examine the effects of pressure and temperature on the concentration limits; all experiments were carried out at a pressure of 750 mm and a temperature of 20° with spark ignition of the mixture.

The ability of the spark to ignite the mixture is determined not only by the composition of the mixture, but also by the characteristics of the source of ignition. At concentrations in the vicinity of the two limits a more powerful spark is necessary for the ignition of the mixture than at concentrations within the explosion range. A weak spark may not ignite a mixture which will burn when a more powerful spark is applied. Hence, in the determination of the concentration limits, it is always necessary to make sure that the spark used is sufficiently powerful. It must be pointed out that the actual energy yielded by a spark is always less than that calculated from the electrical characteristics of the system: Zeldovich and Simonov [9] showed that the efficiency of a spark is not generally more than a few percent.

In order to confirm that our spark had sufficient, or even more than sufficient, energy, we carried out experiments on the limits of flame propagation in a mixture of hydrogen and air with sparks having half and double the energy of the spark that it was proposed to use. These experiments showed that the values of the limits did not vary over this range of energy. Further confirmation of the adequacy of our spark is provided by the close agreement between our results on the limits of flame propagation in hydrogen-air mixtures and similar results obtained in the investigation [3], in which the mixtures were ignited with an open flame.

The apparatus in which flame-propagation limits were determined is shown diagrammatically in Fig. 1. The explosion flask 1, which is provided with a ground-on cap 6 for the reduction of the pressure to atmospheric and the preservation of the flask, is fixed in a wooden box 2, one side of which has been replaced by a thick sheet of Plexiglas so that visual observation of the explosion can be made. Molybdenum electrodes are fused in so as to form a gap in the center of the flask at which the spark ignition of the mixture is effected. The flask is connected through a tap to a vacuum apparatus which enables the flask to be emptied and filled. The mixture of hydrogen and nitrogen oxide was prepared directly in the explosion flask. The flask 1 was first evacuated, some hydrogen was passed in from a cylinder, and then the nitrogen oxide (N_2O and NO from gas holders; NO_2 from the tube 4). The partial pressure of each component was measured with a mercury manometer. The mixture was ignited 5-6 minutes after mixing, this period being adequate to ensure that a uniform mixture was obtained. The spark used for the ignition of the mixture was obtained from a high-tension unit, which is shown diagrammatically in Fig. 1 together with the vacuum part of the apparatus. The high tension (up to 7.5 kV) is obtained from the step-up transformer 7, the output of which is rectified by the kenotron KR-110 8 and passed to the 2-microfarad condenser 9. The cathode of the kenotron is fed from the step-down transformer 10, which has a rheostat in the primary circuit. The condenser is charged, and the operation of the switch 11 will then connect the condenser to the electrodes in the explosion flask (spark gap 2 mm), and the spark discharge of the condenser will occur. The powerfulness of the spark was varied in the experiments by varying the p.d. applied to the primary of the step-up transformer and to the kenotron, and also by varying the length of the spark gap.

The hydrogen used was the commercial gas from a cylinder. Nitrous oxide was prepared by the thermal decomposition of ammonium nitrate, and it was purified from NO and collected over saturated brine, in which N_2O is almost insoluble. Nitric oxide was prepared by the action of hydrochloric acid on sodium nitrate solution in presence of ferric chloride and was also kept in a gas holder over brine. Nitrogen dioxide was prepared from nitric oxide and oxygen. The reaction was carried out in the vacuum part of the apparatus shown in Fig. 1. Nitric oxide was mixed with excess of oxygen in the evacuated glass flasks 3, and the resulting equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide ($2NO_2 \rightleftharpoons N_2O_4$) was pumped off through the trap 5, which was cooled with liquid air; all oxygen was then removed from the system. The mixture was then thawed and was kept as a liquid in the tube 4, which has a ground joint and is connected to the apparatus through a tap.

At room temperature we are dealing with the equilibrium mixture $2NO_2 \rightleftharpoons N_2O_4$ which contains an appreciable amount of N_2O_4. In preparing the mixtures, we always took the measured manometric pressures of the equilibrium mixture as our basis, but in calculating the actual amount of oxygen taking part in the reaction, we made a correction for the equilibrium between nitrogen dioxide and dinitrogen tetroxide, taking into account the vari-

ation of the equilibrium constant with temperature and pressure. Table 1 gives the result of such a calculation for our experimental conditions [T = 20°, p_{total} = 750 mm, the partial pressure of the equilibrium mixture $2NO_2 = N_2O_4$ varied from 75 mm (0.098 atm) to 675 mm (0.88 atm)].

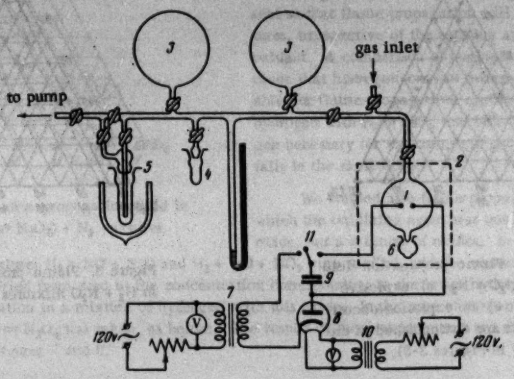

Fig. 1. Diagram of apparatus: 1) explosion flask; 2) wooden box with screen; 3) flasks for the preparation of NO_2; 4) tube for keeping NO_2; 5) trap for reaction products; 6) ground-on cap for reducing pressure after the explosion; 7) step-up transformer; 8) kenotron KR-110; 9) 2-microfarad condenser; 10) step-down transformer; 11) switch.

Experimental Results

Flame-propagation field for H_2—N_2O mixtures. The experimental results on the concentration limits for flame propagation in mixtures of hydrogen and nitrous oxide with and without the addition of an inert diluent (nitrogen) are presented in Fig. 2 in triangular coordinates. Concentrations are expressed as percentages, and can be determined in the usual way for any point on the diagram. The blank circles indicate explosive mixtures, and the black circles indicate mixtures in which no explosion occurred. The flame-propagation field is the area bounded by the horizontal axis and by the curve drawn so as to lie between the rings and the black circles.

It will be seen from Fig. 2 that, in absence of nitrogen, mixtures of hydrogen and nitrous oxide are explosive for a wide range of compositions: from 5.0% to 86.0% N_2O. As the mixture is diluted with nitrogen, the flame-propagation field becomes narrower, and the propagation limits continue to become closer together until, at 75% of nitrogen, flame propagation no longer occurs, irrespective of the relative amounts of hydrogen and nitrous oxide in the mixture. It should be noted that all mixtures containing less then 5% or more than 86% of hydrogen are nonexplosive, irrespective of the relative amounts of the other components (nitrogen and nitrous oxide).

In $H_2 + N_2O$ mixtures diluted with air (Fig. 3), flame propagation again does not occur in mixtures containing less than 5% hydrogen. The upper limit falls somewhat and approximates to 74% of hydrogen, i.e. to the value of the limit for a mixture of hydrogen and air. Fig. 4 shows the flame-propagation fields for mixtures of hydrogen with oxygen and nitrogen, which we determined for comparison. Comparison between Figures 2 and 4 shows that the flame-propagation field for mixtures of hydrogen and nitrous oxide is somewhat narrower than that for mixtures of hydrogen and oxygen, though the difference is not great. The lower limits do not differ appreciably, the main difference being in the upper limits.

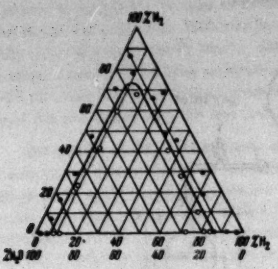

Figure 2. Flame-propagation field for $H_2 + N_2O + N_2$: o) explosive mixtures; •) no explosion occurs (the points are distinguished in the same way in Figures 3-8).

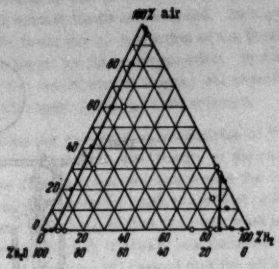

Figure 3. Flame-propagation field in $H_2 + N_2O$ mixtures diluted with air.

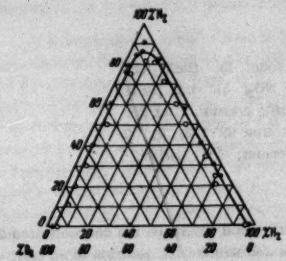

Figure 4. Flame-propagation field in $H_2 + O_2 + N_2$ mixtures.

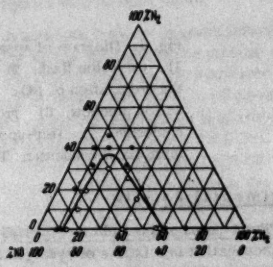

Figure 5. Flame-propagation field in $H_2 + NO + N_2$ mixtures.

Flame-propagation field for H_2—NO mixtures. In Fig. 5 the experimental results on the concentration limits of flame propagation in $H_2 + NO$ mixtures are shown in the same triangular coordinates. The minimum hydrogen concentration at which flame propagation is possible is 11.4% (lower limit), and the maximum concentration is 60% (upper limit).

Dilution with nitrogen narrows the field of explosive compositions, and already at 40% of nitrogen no flame propagation can be observed. Here, therefore, we have an appreciably narrower flame-propagation field than in the case of mixtures of hydrogen with nitrous oxide and oxygen.

Flame-propagation field for H_2—NO_2 mixtures. The experimental results on the concentration limits for flame propagation in $H_2 + NO_2$ mixtures are given in Fig. 6. From right to left along the horizontal axis of this graph, the percentage content of the equilibrium mixture $2NO_2 \rightleftharpoons N_2O_4$ in the final mixture is plotted. By the use of Table 1 it is easy to determine the N_2O_4/NO_2 ratio in the various mixtures with hydrogen. In $H_2 + (2NO_2 \rightleftharpoons N_2O_4)$ mixtures the flame-propagation field is displaced toward higher hydrogen concentrations, the lower concentration limit being 25% of hydrogen, which is considerably higher than for other nitrogen oxides.

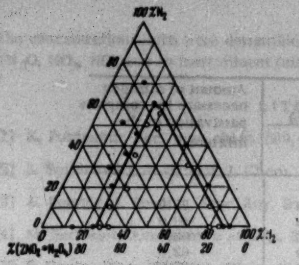

Figure 6. Flame-propagation field in $H_2 + (2NO_2 \rightleftharpoons N_2O_4) + N_2$ mixtures.

The values of the concentration limits for flame propagation in mixtures of hydrogen with nitrogen oxides, air, and oxygen, as determined in the present investigation, are collected in Table 2. In the last column of Table 2 we give the amounts of nitrogen that must be present so that flame propagation will not occur in the mixtures, irrespective of the relative amounts of hydrogen and oxidant. A comparison of our results enables us to conclude that hydrogen-oxygen mixtures are the most favorable for flame propagation, and then follow mixtures of hydrogen with N_2O, NO_2, and NO. The amount of nitrogen necessary for the complete passivation of the mixture falls in the same order.

We studied also flame propagation in mixtures in which the oxidizing agent was not an individual nitrogen oxide, but a mixture of oxides. In this series of experiments the ternary mixtures $H_2 + NO + N_2O$ and $H_2 + NO + NO_2$ were studied, and the content of each individual nitrogen oxide was varied from zero to the concentration corresponding to the lower hydrogen concentration limit for flame propagation in a mixture of hydrogen with this oxide. In the case of mixtures with NO_2, the equilibrium mixture $2NO_2 \rightleftharpoons N_2O_4$ was taken, as before. The results of these experiments are shown in the form of triangular graphs in Figures 7 and 8.

TABLE 1

Compositions of Mixtures of Hydrogen with N_2O_4 and NO_2 for Various Partial Pressures of the Equilibrium Mixture at 20°

Content of equilibrium mixture $2NO_2 \rightleftharpoons N_2O_4$ in final mixture (%)	Partial pressure of equilibrium mixture $2NO_2 \rightleftharpoons N_2O_4$ (atm)	Degree of dissociation (%)	Composition of mixture (%)		
			NO_2	N_2O_4	H_2
10.0	0.098	44.9	6.2	3.8	90.0
20.0	0.200	33.4	10.0	10.0	80.0
30.0	0.294	27.8	12.4	17.6	70.0
40.0	0.39	24.3	15.7	24.3	60.0
50.0	0.49	21.9	17.9	32.1	50.0
60.0	0.59	20.0	20.0	40.0	40.0
70.0	0.69	18.7	21.9	48.1	30.0
80.0	0.78	17.5	23.8	56.2	20.0
90.0	0.88	16.5	25.5	64.5	10.0

Note. The expression for the equilibrium constant is taken from [10]:

$$\log K = -\frac{2692}{T} + 1.75 \log T + 0.00484\,T - 7.144 \cdot 10^{-6} \cdot T^2 + 3.062$$

$$\alpha = \sqrt{\frac{1}{1+\frac{4P}{K}}} \qquad [NO_2] = \frac{2\alpha}{1+\alpha}$$

TABLE 2

Concentration Limits for Flame Propagation

Mixture	Amount of H_2 in limiting mixture (%)		Amount of nitrogen necessary for complete passivation of the mixture
	Lower limit	Upper limit	
H_2+N_2O	5.0	86.0	75.0
H_2+NO	11.4	60.0	40.0
$H_2+(2NO_2 \rightleftarrows N_2O_4)$	24.0	87.6	60.0
H_2+ air	4.0	74.0	62.0
H_2+O_2	4.0	96.0	82.0

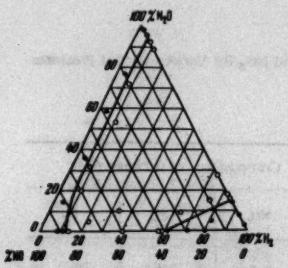

Figure 7. Flame-propagation field for $H_2 + NO + N_2O$ mixtures.

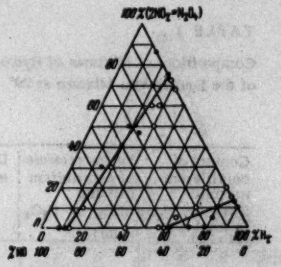

Figure 8. Flame-propagation field for $H_2 + NO + NO_2$ mixtures.

As will be seen from Fig. 7, $H_2 + NO + N_2O$ mixtures are explosive over a very wide field of compositions. As in the case of nitrous oxide, absence of flame propagation is found only in mixtures containing less than 5% and more than 86% of hydrogen. When additions of N_2O are made to mixtures of hydrogen and NO, the flame-propagation field is greatly extended, and already at 15% N_2O the mixture behaves as $H_2 + N_2O$, rather than H_2 + NO.

The flame-propagation field for $H_2 + NO + NO_2$ mixtures is shown in Fig. 8. The overall effect of the introduction of NO_2 into an $H_2 + NO$ mixture is to extend the flame-propagation field fairly considerably; although the lower limit is raised as the NO_2 content of the mixture increases, this is more than counterbalanced by the rise in the upper concentration limit.

If we consider $H_2 + N_2O$ and $H_2 + NO_2$ as our basic mixtures, then on the basis of Figures 7 and 8 we may state that dilution of these mixtures with nitric oxide results in a narrowing of the flame-propagation field in accordance with the closer concentration limits for the $H_2 + NO$ mixtures.

SUMMARY

The concentration limits were determined for flame propagation in mixtures of hydrogen with nitrogen oxides (N_2O, NO_2, NO) and an inert diluent (nitrogen), the components being taken in various proportions.

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PHASE DIAGRAM OF THE BINARY SYSTEM TITANIUM-ALUMINUM

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The phase diagram of the system titanium-aluminum has been investigated by various workers [1-4]. In early investigations [1] alloys of the binary system containing 0-37% of titanium were studied, and there were indications of the existence of the compound $TiAl_3$ (62.7% Al) in the system. The compound $TiAl_3$ melts incongruently and forms a eutectic with aluminum at 0.03% Ti. In later investigations [2-4] titanium-rich alloys of the system were studied. It was shown that, apart from the compound $TiAl_3$, there is an intermediate γ-phase based on the compound TiAl (36.02% Al). This phase is formed by peritectic reaction and has a tetragonal face-centered lattice. In the phase diagrams given in the papers published, liquidus curves and peritectic-equilibrium curves are represented by broken lines.

EXPERIMENTAL

Preparation of Alloys. In the present investigation alloys of the binary system titanium-aluminum containing up to 70% Al were studied by the following methods: thermal analysis, microstructure determination, hardness determination, x-ray structure analysis, heat-stability determination. The alloys were prepared from titanium of 99.5% purity and aluminum of 99.99% purity. Alloys containing up to 37.5% Al were prepared by powder-metallurgy methods, and were then melted in a vacuum induction furnace. The remaining alloys, which contained up to 70% Al, were prepared by the fusion of the pure metals. The change in weight of the samples was checked by weighing them before and after fusion; it was generally less than 0.5% of the weight of the sample.

Thermal Analysis. In studying the fusion diagram with a Kurnakov pyrometer, we recorded cooling curves for alloys containing 20-70% Al. The weight of each sample was 30-40 g. The fusion was carried out in an induction furnace in a current of pure argon. Titanium-rich alloys were melted in thorium dioxide crucibles, and the remainder in corundum crucibles coated with zirconium dioxide. Temperatures were measured with a thermocouple of platinum and platinum-rhodium. For the determination of the crystallization temperatures of alloys containing 97.5%, 95%, and 90% of titanium, a tantalum-tungsten thermocouple was used. The thermal-analysis results are given in Table 1. Figure 1 shows the phase diagram of the binary system titanium-aluminum, constructed on the basis of the experimental results. Three branches of the liquidus curve are shown; these correspond respectively to crystallization of the β solid solution based on titanium, the γ solid solution based on the compound TiAl, and the compound $TiAl_3$. Liquidus branches intersect at temperatures of 1510° and 1400°, corresponding to the peritectic equilibria:

1. β + melt $\rightleftharpoons$ γ at 1510°
2. γ + melt $\rightleftharpoons$ $TiAl_3$ at 1400°

At 600° on the aluminum-rich side of the system eutectic equilibrium occurs with a eutectic point corresponding to 0.03% Ti [1]. Aluminum raises the temperature for the polymorphous transformation of titanium. In order to determine the temperature for the transformation of the α-modification into the β-modification, a differential recording was made with a Kurnakov pyrometer for pure titanium and an alloy containing 2.5% Al in an atmosphere of argon. The following temperatures were found for the beginning of the conversion of the α-phase into the β-phase: for pure titanium 870°, and for the 2.5% Al alloy 930° – values that are in accord with data in the literature.

TABLE 1

Results of Thermal Analysis

Al content (%)	Temperature at halt (°C)		Al content (%)	Temperature at halt (°C)	
	First	Second		First	Second
2.5	1720		37.5		1500
5	1720		45	1490—1470	
10	1710		50	1460—1420	
20	1660		55	1460—1420	
22,5	1660—1610		60		1420—1380
25	1630—1570		62.7	1410	
33	1560	1520	65		1400
35		1500	70	1410	660
36.02		1510			

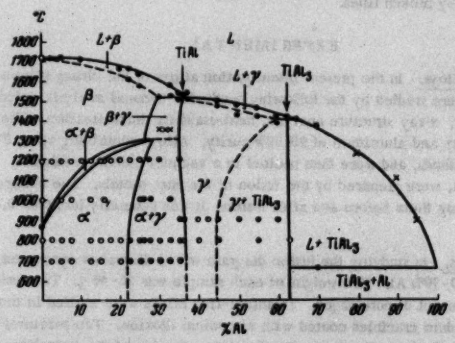

Figure 1. Phase diagram of the binary system titanium-aluminum (fusion diagram plotted from the authors' data).

Microstructure. Microstructure investigations were carried out on cast samples and on samples quenched from various temperatures. The alloys were sealed in silica ampoules under vacuum and subjected to the following thermal treatment:

1) Homogenizational annealing at 1200° for 48 hours and at 1100° for 500 hours, followed by slow cooling in the furnace; or 2) quenching in water after a period of 48 hours at 1200°, or 100 hours at 1000°, or of 200 hours at 800°, or of 330 hours at 700°.

In the thermal treatment, these long periods at constant temperature were essential because a state of equilibrium is attained very slowly in these alloys. Sections were etched with a reagent of the following composition: 1 part of hydrofluoric acid, 1 part of glycerol, and 1 part of nitric acid. Samples having the structure of the α solid solution were etched with sulfuric acid (1 : 1) heated to about 90°. The microstructural analysis of the alloys confirms the thermal-analysis results.

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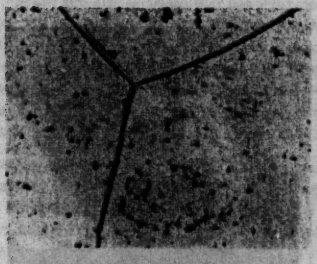

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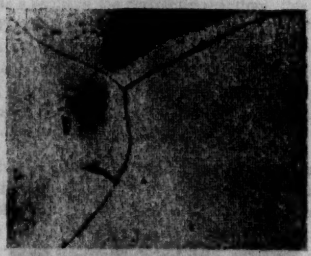

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Figure 2. Cast alloy containing 17.5% Al (x 200).
Figure 3. Alloy containing 15% Al quenched from 1200° (x 200).
Figure 4. Alloy containing 22.5% Al quenched from 1200° (x 200).
Figure 5. Alloy containing 17.5% Al quenched from 800° (x 200).
Figure 6. Alloy containing 22.5% Al quenched from 800° (x 200).
Figure 7. Cast alloy containing 30% Al (x 200).

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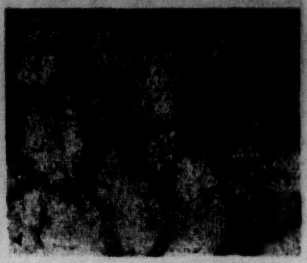

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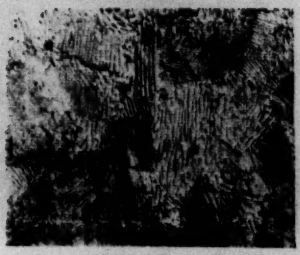

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Figure 8. Cast alloy containing 35% Al (x 200).
Figure 9. Cast alloy containing 28% Al (x 200).
Figure 10. Alloy containing 28% Al quenched from 800° (x 200).
Figure 11. Alloy containing 40% Al quenched from 800° (x 200).
Figure 12. Alloy containing 42% Al quenched from 800° (x 200).
Figure 13. Cast alloy containing 70% Al (x 200).

In systems ranging from pure titanium to an alloy containing 37.5% Al, the phase that first crystallizes from the melt is the β-phase, a solid solution based on β-titanium and having a body-centered cubic lattice. The microstructure of alloys with primary separation of the β-phase in the cast state has the form of long thin plates (Fig. 2).

Alloys quenched from 1200° are shown in Figures 3 and 4. The sample containing 7.5% Al has a disintegrated β-phase, this condition being the result of the instability of this phase under the conditions of quenching. The structure of an alloy in the (α + β) region is shown in Fig. 3 (15% Al): the α-phase is present as light-colored grains, and the disintegrated β-phase as fine needle-shaped segregations. Alloys containing 17.5-25% Al and quenched from 1200° have the polyhedral structure of the α solid solution (Fig. 4). Samples of alloys of the binary system titanium-aluminum quenched from 800° and containing 0-20% Al have the structure of the α solid solution (Fig. 5). An alloy containing 22.5% Al and quenched from 800° shows disintegrated grains of α solid solution and the separation of the γ-phase as a result of the reduction of the solubility of aluminum in titanium with lowering of temperature (Fig. 6). At 1510° a peritectic reaction occurs in the system between crystals of β-phase containing 29.5% Al and melt containing 37.5% Al with formation of the γ solid solution based on the compound TiAl.

Fig. 7 shows the structure of the cast alloy containing 30% Al; it consists of primary crystals of disintegrated β solid solution, which are surrounded by γ-phase in the form of streaks. The 35% Al alloy contains residues of undissolved α'-phase and also γ-phase that has separated as a result of the peritectic reaction; this has the form of grains, which appear darkly colored in the photograph (Fig. 8). At a temperature of about 1300° (determined by the method of quenching samples from temperatures above and below this), a peritectoid reaction occurs in the system. Peritectoid transformation is undergone by alloys containing 26-35% Al. In the case of the 28% Al alloy we may follow the course of the peritectoid reaction. Fig. 9 shows a cast sample of the 28% Al alloy from the (β + γ) region, and Fig. 10 shows the same sample quenched from 800°. It can be seen from Fig. 10 that the alloy underwent transformation while in the solid state; the (α + γ) phase is present.

A similar structure is possessed by all alloys containing 27.5-35% Al and quenched from temperatures below the temperature of the peritectoid transformation. Alloys in the γ-phase region have a characteristic microstructure, which is shown in Fig. 11 (it consists of grains of γ solid solution). In the range of 60-65% Al a second peritectic reaction occurs at 1400° between the melt and solid γ-phase with formation of the compound $TiAl_3$. The microstructure of an alloy from the two-phase region (γ + $TiAl_3$) is shown in Fig. 12; it consists of grains of γ solid solution and needle-shaped segregations of the compound $TiAl_3$ (the latter is brittle in the pure state). Fig. 13 shows the microstructure of a sample containing 70% Al: the eutectic and the primary plates of the compound $TiAl_3$ can be seen.

Hardness of the Binary Alloys. Samples of alloys submitted to various thermal treatments were tested for hardness in a Vickers apparatus by means of a diamond pyramid under a load of 10 kg. Alloys containing 60% or more of aluminum were tested for hardness in the cast state. The results obtained are given in Table 2 and represented graphically in Fig. 14. The curves show that, as the solubility limit of aluminum in titanium is approached, the hardness of the alloy rapidly increases. The increase in hardness continues up to the (α + γ) two-phase boundary. Beyond the solubility limit of the solid solution the hardness diminishes, and in the region of the compound TiAl it has a minimum value. In the single-phase region of the γ solid solution, the hardness varies according to a curve that is turned with its convex side upwards; in the two-phase region (γ + $TiAl_3$) it rises slightly up to the composition of the compound $TiAl_3$. From the composition corresponding to the compound $TiAl_3$ the hardness falls sharply down to the value for pure aluminum. The hardness curve in the region of alloy compositions that have been studied inadequately is represented by a broken line.

X-Ray Structure Investigation. The structures of the alloys were investigated by the x-ray method in the Department of Aviation Materials of the Zhukovsky Air Force Engineering Academy in collaboration with A. Ya. Snetkov. The powders for investigation were obtained by grinding samples that had been given prolonged annealing at 800°. The experimental samples were prepared from the powders by cold hammering and further annealing in sealed silica tubes at 800° for 24 hours. The measurements were made in a Debye camera (d = 57.4 mm), and also in a Sachs camera for reflection pictures. Iron radiation was used in the Debye camera, and from the photographs obtained the phase composition and type of crystal structure were determined by the asymmetry method. Copper radiation was used in the Sachs camera, and from the photographs obtained the parameters a and c of the lattice of the α solid solution were determined.

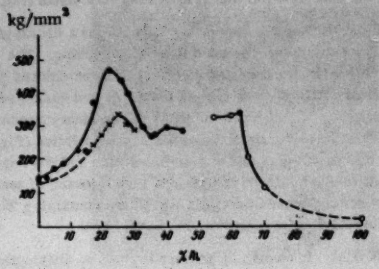

Figure 14. Graph showing the relation between Vickers hardness of alloys of the binary system titanium-aluminum and composition: •) queriched from 800°; x) quenched from 1200°; o) cast.

x-Ray photographs of alloys containing 0-28% Al taken in the Debye camera had one system of lines corresponding to a close-packed hexagonal lattice (phase α). The x-ray photograph of the 28% Al alloy showed the existence of two phases, one having a hexagonal lattice (α) with close packing, and the other a tetragonal face-centered lattice (γ).

x-Ray photographs of alloys containing 32.5-50% Al showed lines corresponding solely to one tetragonal lattice (phase γ). A summary of lattice-parameter measurements for the α-phase is given in Table 3.

Figure 15 gives a graphical representation of the effect of the aluminum content on the parameters of the close-packed hexagonal lattice. As the aluminum content of the alloy increases, the lattice constants a and c of the α solid solution diminish greatly and the ratio c/a increases (Fig. 15). When the saturation limit of the solid solution is reached, the lattice parameters a and c remain constant. Near the solubility limit the curves for the relation between the lattice parameters of the α solid solution and the aluminum concentration become less steep, but their slopes are greater than those found in the investigation of Bumps, Kessler, and Hansen [3]. Unlike these authors, we determined the limiting aluminum concentration in the α aluminum-titanium solid solution by the x-ray method (21.6% Al at 800°).

TABLE 2

Vickers Hardness of Alloys of the Binary System Ti—Al at p = 10 kg

Al content (% by weight)	Vickers hardness (kg/sq.mm) Quenched from 800°	Quenched from 1200°	Al content (% by weight)	Vickers hardness (kg/sq.mm) Quenched from 800°	Quenched from 1200°	Al content (% by weight)	Vickers hardness (kg/sq.mm) Cast alloys
0	150	131	26	442		55	327
2.5	146		27.5	434	302	60	333
5	176		28	403		62.7	334
7.5	187	164	30		285	65	207
10	127		32.5	299		70	116
12.5	232	221	35	272		100	15.5
15	228		36.02	279			
17.5	373		40	299			
22.5	433		45	283			
25	381	366					

Investigation of Heat Stability. We are the first to investigate the heat stability of alloys of the titanium-aluminum system; we used the centrifugal method [5] at 550° under a stress of 15 kg/sq.mm. The aluminum contents of the alloys investigated varied from zero to 27.5%. The deformation time at 550° was 250 hours, and then 50 hours was given at 600° under the same stress. The bending deformations of the binary alloys under the action of a centrifugal force are given as a function of aluminum content in Table 4 and Figures 16 and 17. As a measure of heat stability we took the linear bending displacement in millimeters, considered as a function of time, and also the time for the attainment of a given linear displacement (2 and 4 mm) as a function of the aluminum content of the alloy. Investigation showed that, under these test conditions, the heat stability of the alloys increases as the aluminum content of the α-titanium solid solution increases. It is characteristic here that the heat-stability of the alloys increases up to 20-21% Al, i.e. up to the aluminum concentration corresponding to the solubility

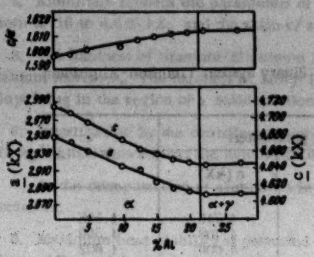

Figure 15. The effect of aluminum on the parameters of the hexagonal lattice of the α-phase in the system Ti—Al.

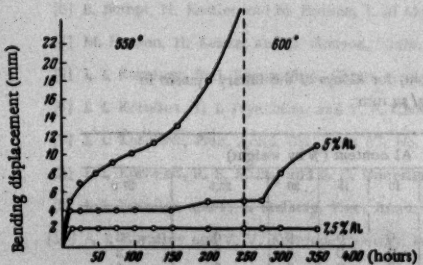

Figure 16. Heat-stability of the binary system titanium-aluminum as a function of the aluminum content (0, 5, 7.5%) at σ = 15 kg/sq.mm.

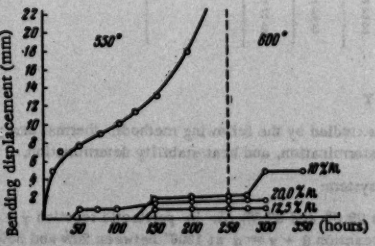

Figure 17. Heat-stability of the binary system titanium-aluminum as a function of the aluminum content (0, 10, 20, 12.5%) at σ = 15 kg/sq.mm.

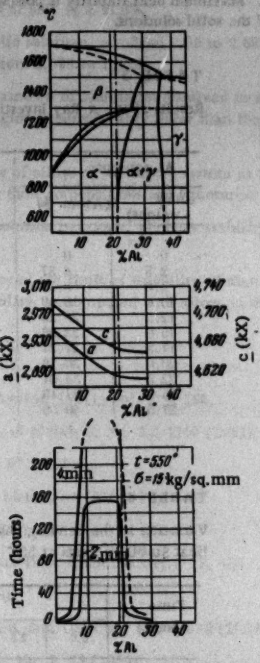

Figure 18. Phase diagram and composition-property diagrams of the system titanium-aluminum.

limit in α-titanium. Alloys of the two-phase region (α + γ) containing 22.5% and 27.5% Al were found to be less heat-stable than alloys containing 15-21% Al. Figure 18 shows the solubility diagram for aluminum in titanium in juxtaposition with diagrams for crystalline-lattice parameters and for time of attainment of bending displacements of 2 mm and 4 mm in the heat-stability test.

It will be seen from Fig. 18 that, for moderate test temperatures, there is a definite relationship, which has been observed in some other metal systems [6-10], between heat-stability, chemical composition, and structure of alloys of the binary system titanium-aluminum. Alloys lying in the region of solid solutions at the limit of saturation have higher heat-stability than pure titanium or unsaturated solid solutions based on tita-

nium. Maximum heat stability is possessed by alloys having compositions in the vicinity of the saturation boundary of the solid solutions.

TABLE 3

Results of the x-Ray Investigation of Alloys of the Binary System Titanium-Aluminum

Al content (% by weight)	Al content (Atom-%)	Phases	Lattice parameters a (kX)	Lattice parameters c (kX)	c/a
0	0	α	2.950	4.716	1.598
2.5	4.37	α	2.944	4.708	1.599
5.0	8.53	α	2.932	4.696	1.602
10.0	16.49	α	2.915	4.676	1.604
12.5	20.25	α	2.901	4.664	1.608
15.0	23.86	α	2.895	4.658	1.609
17.5	27.37	α	2.888	4.652	1.611
20.0	30.76	α	2.885	4.649	1.612
22.5	34.01	α	2.880	4.645	1.613
25.0	37.19	α+γ	—	—	—
27.5	40.09	α+γ	2.881	4.647	1.613

TABLE 4

Variation in the Bending Displacement (mm) for Alloys of the Binary System in Heat Stability Tests at 550° and σ = 15 kg/sq.mm

Time (hours)	Al content (% by weight)								
	0.0	2.5	5	7.5	10	15	20	22.5	27.5
0	0	0	0	0	0	0	0	0	0
2	3	1	2	2	0	0	0	3	2
5	4	2	2	2	0	0	0	3	4
10	6	2	4	2	0	0	0	4	5
15	6	2	4	2	0	0	0	Collapse	6
25	6	2	4	2	0	0	0		Collapse
50	6	2	4	2	0	0	1		
75	6	2	4	2	0	0	1		
100	6	2	4	2	0	0	1		
150	7	5	4	2	2	2	2		
200	7	5	5	2	2	2	2		
250	8	6	6	2	2	2	2		
275*	18	10	10	2	2	2	2		
300*	45	11	11	2	2	3	2		

* At 600°

SUMMARY

1. The phase diagram of the binary system Ti—Al was studied by the following methods: thermal analysis, microstructure analysis, x-ray structure analysis, hardness determination, and heat-stability determination.

2. The following transformations occur in the Ti—Al system:

a) peritectic reaction β + melt ⇌ γ at 1520° between 29.5% and 37.5% Al; b) peritectic reaction γ + melt ⇌ $TiAl_3$ at 1400° between 60% and 64% Al; c) peritectoid reaction β + γ ⇌ α at 1300° between 28% and 35% Al; d) temperature for the conversion of α-phase into β-phase rises from 870° at 0% Al to 1300° at 27.5% Al.

3. At 1200° the solubility of aluminum in titanium is 26%, and at 800° it is 21.6%.

4. Aluminum reduces the parameters of the lattice of the α solid solution: a - from 2.95 to 2.881 kX; c - from 4.716 to 4.646 kX; and the ratio c/a rises almost linearly from 1.598 to 1.613.

5. The hardness of titanium-aluminum alloys increases as the amount of aluminum dissolved in the α-phase of titanium increases. The hardness of alloys lying in the γ-phase region is considerably lower than the hardness of alloys lying in the region of α solid solution.

6. Investigation by the centrifugal method of the heat stability of alloys of the binary system at 550° and σ = 15 kg/sq.mm showed that the heat stability of alloys depends on their compositions and structures.

7. As the concentration of aluminum in the α-titanium solid solution increases, the heat stability of the alloy increases.

8. Maximum heat stability is possessed by alloys in the vicinity of the limit of solubility of aluminum in titanium. Alloys of the (α + γ) two-phase region have low heat stability, as compared with alloys in the region of solid solutions.

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EFFECT OF TEMPERATURE ON THE DIFFUSION CURRENT AND THE THICKNESS OF THE DIFFUSION LAYER

V. V. Gerasimov and I. L. Rozenfeld

Diffusion is the controlling factor in many corrosion processes associated with depolarization by oxygen. Several studies of the mechanism of the reduction of oxygen have appeared [1-4], but the effect of temperature has not been investigated. It was considered to be of interest to investigate the temperature dependence of the limiting diffusion current and the thickness of the diffusion layer. The theory of the transfer of a substance in a stirred solution, as developed by Levich [5], enables us to calculate the thickness of the diffusion layer (δ) and the limiting diffusion current (I_d).

$$\delta = 1{,}63 \cdot D^{\frac{1}{3}} \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}}; \quad (1)$$

$$I_d = 0{,}617\, nFD^{\frac{2}{3}} \nu^{-\frac{1}{6}} \omega^{\frac{1}{2}} c, \quad (2)$$

in which D is the diffusion coefficient, ν is the kinematic viscosity of the solution, ω is angular velocity, c is the concentration of the diffusing substance, n is the number of electrons taking part in the reaction, and F is the faraday number.

In the present investigation we studied the effect of temperature on δ and I_d. Measurements were carried out with a rotating copper electrode in a solution containing $FeCl_3$ (0.005 N) and HCl (0.1 N) and with a rotating amalgamated copper electrode in N NaCl. In all the experiments the rate of stirring was 1500 r.p.m. The measurements were carried out by the method developed by Kabanov and Siver [6].

EXPERIMENTAL

In the region of oxygen depolarization, the cathodic polarization curves obtained at an amalgamated copper electrode in N NaCl (Fig. 1) have two inflections. The first inflection corresponds to the reaction of hydrogen peroxide formation:

$$O_2 + 2H_2O + 2e \longrightarrow H_2O_2 + 2OH^-; \quad (3)$$

and the second inflection corresponds to the ionization of oxygen to hydroxyl ions:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-. \quad (4)$$

The potentials at which the inflections corresponding to Reactions (3) and (4) occur on the polarization curves are in close accord with the values obtained by Tomashov [2] and Kolthoff and Miller [7].

Tables 1 and 2 give values of I_d and δ, as calculated from Formulas (1) and (2) and as determined experimentally. Values of ν were taken from tables [8], and the oxygen concentration from data in the literature [8, 9]. The diffusion coefficient of ferric chloride at 20° was calculated from the experimentally determined value of I_d by means of Equation 2; for other temperatures it was calculated from Torre's data [10]. The diffusion coefficient of oxygen was calculated from the equation:

$$D = \frac{kT}{6\pi r}, \tag{5}$$

in which k is Boltzmann's constant, T is the absolute temperature, and r is the radius of the diffusing molecule. The value of r was determined from the value of D_{O_2} at 18° by means of Equation 5. The value of D_{O_2} was obtained by extrapolation of Landolt's data [3]. The experimental values of δ were obtained with the aid of the equation:

$$\delta_{expt} = \frac{nFCD}{I_{d_{expt}}}. \tag{6}$$

TABLE 1

Effect of Temperature on the Thickness of the Diffusion Layer at a Rotating Copper Electrode (1500 r.p.m.) in a Solution of $FeCl_3$ (0.005 N) and HCl (0.1 N)

Temperature (°C)	D (x 10^{-5} cm^2/sec)	ν (x 10^{-2} poise)	Calculated values		Experimental values	
			I_d (ma/sq.cm)	δ (x 10^{-3} cm)	I_d (ma/sq.cm)	δ (x 10^{-3} cm)
20	0.51	1.05	6.8	1.06	6.80	1.06
40	0.72	0.656	9.9	1.08	10.0	1.07
50	0.85	0.549	11.7	1.09	12.0	1.06
80	1.35	0.356	16.7	1.18	17.0	1.16
30	0.623					

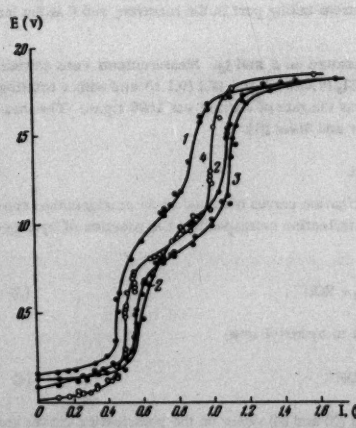

Figure 1. Cathodic polarization curves for a rotating amalgamated electrode in N NaCl (1500 r.p.m.): 1) 95°; 2) 80°; 3) 50°; 4) 20°.

It follows from Tables 1 and 2 that the calculated values of δ and I_d are in close agreement with the experimental values. In solutions containing $FeCl_3$ (0.005 N) and HCl (0.1 N), the depolarizer concentration is constant and I_d increases almost linearly with temperature. In N NaCl the oxygen concentration falls with rise in temperature and I_d passes through a maximum. The thickness of the diffusion layer increases with temperature. Analysis of Equation 1 shows that δ is more greatly dependent on the diffusion coefficient than on the viscosity (the power index of D is 1/3, whereas that of viscosity is 1/6). The diffusion coefficient increases with rise in temperature, and, for constant stirring conditions, the thickness of the diffusion layer also increases:

$$\frac{\delta_{80}}{\delta_{20}} = \frac{1.62\omega^{-\frac{1}{2}} D_{80}^{\frac{1}{3}} \nu_{80}^{\frac{1}{6}}}{1.62\omega^{-\frac{1}{2}} D_{20}^{\frac{1}{3}} \nu_{20}^{\frac{1}{6}}} =$$

$$= \left(\frac{D_{80}}{D_{20}}\right)^{\frac{1}{3}} \left(\frac{\nu_{80}}{\nu_{20}}\right)^{\frac{1}{6}} = 1.4 \cdot 0.79 = 1.1. \tag{7}$$

The ratio of the experimentally determined values of δ_{80} and δ_{20} is 1.095.

TABLE 2

Effect of Temperature on the Thickness of the Diffusion Layer at a Rotating Amalgamated Copper Electrode (1500 r.p.m.) in N NaCl

Temperature (°C)	D_{O_2} ($\times 10^5$ cm²/sec)	$\nu^{1/6}$ ($\times 10^{-2}$ poise)	Calculated values, n = 2: I_d (ma/cm²)	Calculated values, n = 4: I_d (ma/cm²)	Calculated values: $\delta \times 10^3$ cm	Experimental values, n = 2: I_d (ma/cm²)	Experimental values, n = 2: δ ($\times 10^3$ cm)	Experimental values, n = 4: I_d (ma/cm²)	Experimental values, n = 4: δ ($\times 10^3$ cm)	Oxygen Concentration ($\times 10^{-7}$ mole/cc)
20	1.97	1.087	0.508	1.016	1.64	0.5	1.66	1.00	1.66	2.18
50	3.90	0.610	0.580	1.16	1.87	0.56	1.93	1.12	1.93	1.44
80	6.5	0.402	0.605	1.21	2.07	0.60	2.08	1.10	2.26	1.00
95	8.0	0.340	0.447	0.895	2.15	0.45	2.13	0.9	2.13	0.625

TABLE 3

Values of n at Different Temperatures (1500 r.p.m.)

Temperature (°C)	Copper: I_d (ma/sq.cm)	Copper: n	Iron: I_d (ma/sq.cm)	Iron: n
20	0.8	3.15	0.64	2.53
50	0.89	3.17	0.77	2.65
80	0.74	2.45	0.65	2.15
95	0.5	2.23	0.50	2.23

Investigation of the kinetics of the cathodic process shows that at rotating copper and iron electrodes in N NaCl the values of I_d (Table 3) are lower at all temperatures than the values calculated and obtained experimentally at an amalgamated electrode for the reduction of oxygen according to Equation 4 (n = 4), and are greater than for values calculated for Equation 3; this can be seen from an examination of Table 2. This indicates that, under the given conditions, reduction of oxygen at copper and iron goes partly according to Equation 3, with formation of hydrogen peroxide, and partly according to Equation 4. A similar phenomenon was noted by Kabanov and Siver [6].

The view that the reduction in the value of the limiting diffusion current at copper and iron in N NaCl (as compared with I_d for n = 4) is the result of the screening of part of the surface by oxide films must be rejected on account of the following considerations. The equilibrium potential for the cathodic reduction reactions of Cu_2O, CuO, and $Cu(OH)_2$ in a neutral medium is 0.053-0.19 v [2]. It follows from Fig. 2 that a copper electrode is polarized to potentials that are more negative then 0.1 v. At these potentials the oxides and hydroxides of copper must be reduced. The coincidence between the forward and reverse courses of the cathodic polarization curves for copper (Fig. 2) confirms this view. The behavior of iron is similar (Fig. 3). Tomashov [2] also has noted that at potentials of from −1.0 to −1.2 v oxides on copper and iron are reduced.

At present no theory exists that will enable us to calculate δ in an unstirred electrolyte. Table 4 gives the values of δ calculated by means of Equation 6 from values of I_d measured experimentally at platinum in a solution containing $FeCl_3$ (0.0047 N) and HCl (0.1 N) and at copper and iron in N NaCl in an open system and in a closed system (in which the oxygen concentration does not change with temperature). Table 4 shows that, as the temperature rises, δ diminishes from, on the average, 0.05 cm at 20° to 0.025 cm at 95°. It follows from Fig. 4 that, as a first approximation, we can assume a linear relationship between log δ and 1/T:

$$\log \delta = 1.11 + \frac{476}{T}, \quad (8)$$

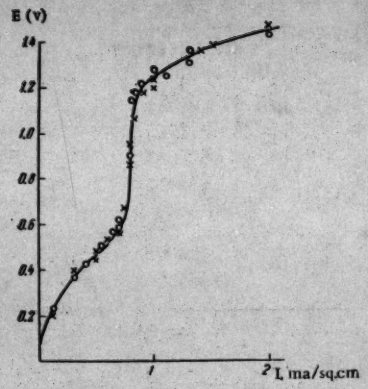

Figure 2. Cathodic polarization curves for copper in N NaCl at 1500 r.p.m.: o) forward course; x) reverse course.

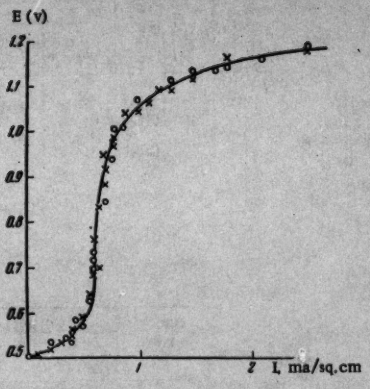

Figure 3. Cathodic polarization curves for iron in N NaCl at 1500 r.p.m.: o) forward course; x) reverse course.

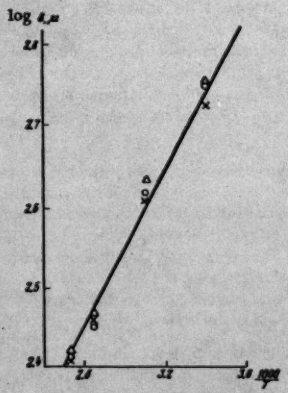

Figure 4. Temperature dependence of the thickness of the diffusion layer in unstirred electrolytes, from Equation 8 and from experimental data: o) copper in N NaCl (open system); Δ) copper in N NaCl (closed system); x) iron in NaCl (open system).

As the temperature rises in an unstirred electrolyte, the value of δ is affected by two opposing factors: 1) as a result of changes in the diffusion coefficient and viscosity δ tends to increase; 2) as a result of the increased mixing resulting from convection δ tends to diminish. The second is the deciding factor. The extent of convectional mixing at a given temperature is not strictly constant and, in each individual case, will depend on the conditions of thermostating, the form and dimensions of the vessel and sample, the rate at which the electrolyte evaporates, etc. As a result, the values of δ are not strictly reproducible, and there are therefore considerable discrepancies between the results of different investigators [2, 11-13].

SUMMARY

1. An investigation was made of the effect of temperature on the limiting diffusion current and the thickness of the diffusion layer at copper, iron, and amalgamated copper electrodes in stirred and unstirred solutions of sodium chloride and ferric chloride.

2. In unstirred electrolytes at constant oxygen concentration the limiting diffusion current increases with temperature. When the concentration of oxygen changes as a result of reduction of solubility with rise in temperature, the limiting current attains its maximum value at 80° and then falls.

TABLE 4

Effect of Temperature on the Thickness of the Diffusion Layer in Unstirred Electrolytes

Temperature (°C)	Platinum in $FeCl_3$ (0.0047 N) + HCl (0.1 N)		N NaCl							
			Copper				Iron			
			Open System		Closed System		Open System		Closed System	
	I_d (ma/cm²)	δ (cm)	I_d (ma/cm²)	δ (cm)	I_d (ma/cm²)	δ (cm)	I_d (ma/cm²)	δ (cm)	I_d (ma/cm²)	δ (cm)
20	0,145	0,047	0,023	0,056	0,023	0,056	0,02	0,052	0,02	0,052
30	0,209	0,042								
40	0,275	0,0365								
50	0,35	0,034	0,040	0,042	0,055	0,046	0,035	0,041	0,045	0,048
80	0,61	0,028	0,055	0,028	0,105	0,029	0,048	0,028	0,081	0,036
95			0,043	0,0256	0,145	0,026	0,042	0,0256	0,110	0,033

3. In a stirred electrolyte the thickness of the diffusion layer increases with rise in temperature. In unstirred electrolytes δ diminishes with rise in temperature as a result of increased convectional mixing.

4. At iron and copper in N NaCl oxygen is reduced partly to hydrogen peroxide and partly to hydroxyl ions.

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EFFECT OF STEAM AND COMPRESSION TREATMENTS ON THE MACROSTRUCTURE AND CATALYTIC ACTIVITY OF ALUMINA

I. E. Neimark, L. Kh. Freidlin, A. I. Rastrenenko, and N. V. Borunova

Difficultly reducible metal oxides are often used as catalysts and also as carriers of catalysts, their function then being to increase the catalyst surface and preserve the catalyst from recrystallization at high temperatures. The causes of the aging of metal oxides have not yet received adequate study. The question of the effect of steam on aging processes in metal oxides is particularly deserving of attention, for water is liberated when the hydroxide of a metal is converted into the oxide, and it is very frequently found as a foreign substance in chemical reactions.

Ormont [1] states that aging processes, which he denotes conventionally by $[S] \rightarrow [S]_n$, proceed with reduction in free energy in all temperature ranges, and foreign substances may either accelerate or retard aging. Maslyansky and Shenderovich [2] found that reduction under pressure of molybdenum trioxide with hydrogen containing 2% of water vapor gave completely inactive brown dioxide. Bohm [3], Fricke and Severin [4], and Weitbrecht and Fricke [5] carried out x-ray and electron microscope studies of changes in the structure of alumina and clays resulting from the action of steam.

In the present investigation the effect of steam on the macrostructure of alumina was studied by adsorption and catalysis methods. The results of this study show that treatment of alumina with steam at 350° results in far-reaching changes in its macrostructure. It is probable that in the course of this treatment the micellar aggregates forming the skeleton of the gel become coarser, the fine pores disappear, and the predominant radius of the intermediate pores increases. It was found that, after the steam treatment, the specific surface of the alumina was reduced from 355 to 125 sq.m/g. In absence of steam, a reduction in the specific surface of alumina of this magnitude is attained only by ignition at temperatures of about 1000° [6]. It was found that, at the same time, there was a reduction in the catalytic activity of the alumina in dehydration reactions. It is probable that the deactivation of alumina is due to its recrystallization in presence of steam at high temperatures and pressures.

It is important to note, therefore, that in processes carried out under pressure in presence of steam the structures of oxide catalysts and carriers may undergo considerable change. Treatment with steam may serve as a method for controlling the porosity properties of oxide catalysts and carriers.

Recrystallized coarse-pore oxide catalysts will probably be of low activity in reactions at relatively low temperatures, but they may be more active in reactions at high temperatures, the rates of which are often limited by diffusion processes. It is natural to suppose that the low specific surface of natural silicates, as compared with artificially prepared silicates, is to be associated with prolonged periods in contact with steam under the pressures existing in rocks.

We also studied the effect of compression at 20,000 atm on the macrostructure of alumina. The results of this study indicate that compression destroys the intermediate pores of alumina and reduces its specific catalytic activity.

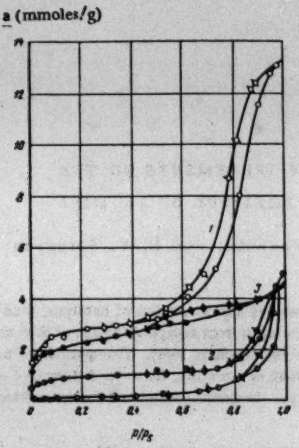

Figure 1. Sorption isotherms for methyl alcohol vapor on alumina samples:
1) Untreated original sample; 2) sample treated with steam; 3) sample compressed at 20,000 atm.
The lowest curve is the benzene isotherm for the sample treated with steam. Desorption points are denoted by short lines.

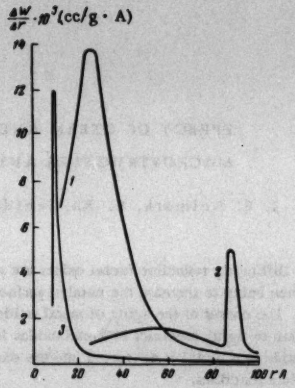

Figure 2. Curves for the distribution of the volume of intermediate pores of alumina samples with respect to effective pore radius:
1) Untreated original sample; 2) sample treated with steam; 3) sample compressed at 20,000 atm.

EXPERIMENTAL

Change in the Macrostructure of Alumina During Treatment with Steam

Alumina powder was heated at 350° in steam at 100 atm in an autoclave for five hours, and it was then formed into 3 x 3 mm grains. In order to establish the structural characteristics of the treated and untreated alumina samples, determinations were made of their apparent densities, their static activities with respect to benzene and methyl alcohol, and their sorption and desorption isotherms for benzene and methyl alcohol vapors, which were determined with the aid of a quartz spring balance in a vacuum apparatus.

Figure 1 shows isotherms for the sorption and desorption of methyl alcohol vapor on samples of alumina, namely, a sample that was not treated with steam (1) and a sample that was treated with steam (2); for the second sample the benzene isotherm is also shown. Adsorption is expressed in millimoles per gram. Fig. 2 shows the calculated curves for the distribution of volume of pores with respect to effective pore radius.

The table gives structural characteristics of the alumina samples investigated, namely, apparent density δ, total volume of pores V_{Σ}, calculated from the difference between the apparent and true densities, volume V_s of liquid benzene and methyl alcohol sorbed from the saturated vapors, and values of the radii corresponding to the maxima on the curves for the distribution of the volume of pores with respect to effective pore radius. The specific surface was calculated from the adsorption isotherm expressed in the linear coordinates of the BET (Brunauer, Emmett, and Teller) equation and also from the value of the adsorption at $p/p_s = 0.1$ by Kiselev's method. The specific surface values given in the table have been averaged; it is these values that were used in the calculations.

TABLE

Structural Characteristics of Alumina Samples (True Density = 3.02 g/cc)

Sample	Apparent Density δ (g/cc)	Total pore Volume V_Σ (cc/g)	Sorption from saturated vapors at 20° V_s (cc/g)		Specific surface (sq.m/g)	Predominant radius or intermediate pores r(A)
			for CH_3OH	for C_6H_6		
1-original, untreated	0.89	0.79	0.50	0.54	355	30
2-treated with steam	0.91	0.77	0.42	0.41	125	90
3-compressed at 20,000 atm	2.20	0.12	0.12	0.12	280	10

It will be seen from the table and figures that the steam treatment brought about a great change in the structure of the alumina: the specific surface was reduced almost to one-third of its original value, and the predominant pore radius increased from 30 to 90 A. On the original sample (Isotherm 1) sorption proceeded both by adsorption in micropores of small radius (less than 10 A), and also by capillary condensation in intermediate pores at comparatively high relative pressures; on the steam-treated sample (Isotherm 2) absorption of methyl alcohol vapor proceeded mainly by capillary condensation (pores for which $\bar{r}$ was about 90 A).

Variation of the Acitivity of Alumina in the Dehydration of Formic Acid

A study was made of the activity of alumina for the dehydration of 85% formic acid passed at a space velocity of 1.5 $hour^{-1}$. The degree of conversion of the acid was determined from the yield of gas from 1 ml of acid. It will be seen from Fig. 3 that steam treatment of the alumina greatly reduced its activity. The reaction temperature had to be raised to almost 100° in order to effect the same degree of decomposition as that obtained over an untreated sample. This lowering of activity is in accord with the great reduction in the specific surface of the alumina brought about by steam treatment.

Figure 4 gives the specific catalytic activities of samples of alumina for this reaction, as calculated for 1 sq. m of surface. This figure shows that their specific activities differ insignificantly below 300°. Above 300°, the activity of the untreated sample remains almost unchanged, but that of the steam-treated sample rises sharply. It is clear that these differences in behavior between the two samples of alumina are associated with difference in macrostructure. Under the action of steam the predominant radius of intermediate pores was tripled, so that the surface of the sample became more accessible and more completely utilized in the reaction.

Variation of the Activity of Alumina in the Dehydration of Ethyl and Isopropyl Alcohols

In presence of the alumina that was not treated with steam, ethyl alcohol was already dehydrated at a measurable rate at 270°. At 310° 93.3% conversion was attained (space velocity 0.12 $hour^{-1}$). When ethyl alcohol was passed over a sample of the same alumina that had been pretreated with steam, no dehydration occurred, even at 400-425°. Steam treatment of the alumina reduced its activity also for the dehydration of isopropyl alcohol (Fig. 5).

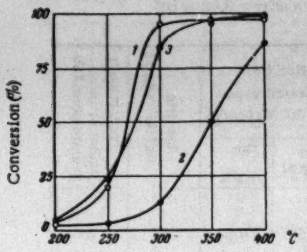

Figure 3. Catalytic decomposition of formic acid over samples of alumina: 1) Original; 2) pretreated with steam; 3) compressed at 20,000 atm.

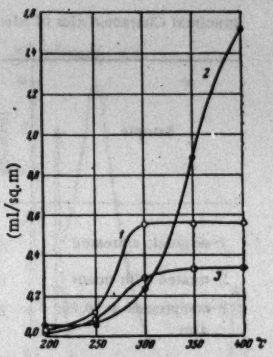

Figure 4. Catalytic activity of alumina samples in the decomposition of formic acid, calculated for 1 sq. m of surface: 1) Original sample; 2) sample pretreated with steam; 3) sample compressed at 20,000 atm.

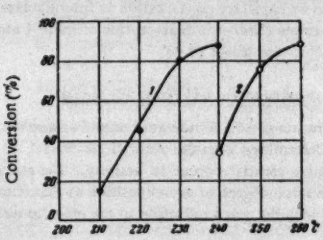

Figure 5. Catalytic dehydration of isopropyl alcohol in presence of samples of alumina: 1) Untreated; 2) pretreated with steam.

Effect of Compression on the Macrostructure and Catalytic Activity of Alumina

Alumina was compressed at 20,000 atm in the special pressure multiplier described previously [7]. The structural characteristics of the compressed sample are given in the table and represented in Figures 1 and 2 (Curves 3). It will be seen from the table and Figures 1 and 2 that, in the compression process, the apparent density of the alumina was increased by a factor of almost 2.5 and the volume of intermediate pores was reduced by a factor of five, this being indicated by the reduction in the size of the hysteresis loop (Fig. 1). The specific surface was reduced from 355 to 280 sq.m/g, and the effective pore radius from 30 to 10 A. Hence, under mechanical treatment it is mainly the intermediate pores that are broken down. These results are in accord with our previous results on the change in the macrostructure of silica gel when subjected to high pressure [8].

Figure 3 shows that both catalysts (compressed and uncompressed alumina) have almost the same activity for the dehydration of formic acid, as calculated for unit volume; their specific activities, calculated for 1 sq. m of surface, differ inappreciably at low temperature. At higher temperatures compressed alumina is appreciably

less active than uncompressed (Fig. 4). It is obvious that these differences in activity are associated with differences in the character of the porosity of the catalysts. In the compressed sample the porous structure is based mainly on micropores (r less than 10 A), and intermediate pores, having been destroyed under the superhigh pressure, are almost absent, as can be seen by comparing ordinates on the curves showing the relation between $\frac{\Delta W}{\Delta r}$ and r. The insufficiency of the number of intermediate pores results in diffusional retardation of reaction.

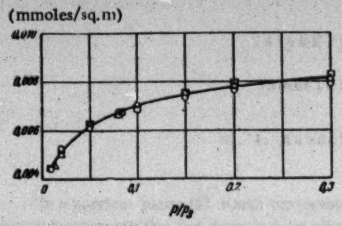

Figure 6. Sorption isotherms for methyl alcohol vapor on samples of alumina, calculated for unit surface (1 sq.m):
o) Original; Δ) steam-treated; □) compressed.

The identity in nature of the activities of the adsorbing surfaces of uncompressed, compressed, and steam-treated alumina is indicated by the coincidence of the absolute adsorption isotherms for methyl alcohol vapor, as calculated for unit surface of the adsorbent (Fig. 6).

SUMMARY

1. The effects of treatment with steam and of compression at 20,000 atm on the macrostructure and catalytic activity of alumina were investigated.

2. It was shown that steam treatment resulted in reduction of the catalytic activity of alumina, great reduction of its specific surface, almost complete disappearance of the micropores, and increase of the volume of intermediate pores. Steam treatment can be used as a method for the control of the porous character of oxide catalysts.

3. Compression results in increase of the apparent density of alumina: the intermediate pores are destroyed, and this causes lowering of the specific catalytic activity of alumina at high temperatures; the reaction is then subject to diffusional retardation.

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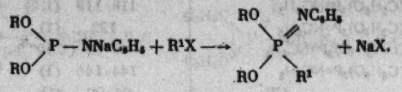
TRIALKYL PHOSPHORIMIDATES

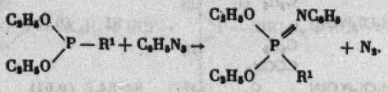
TRIALKYL PHENYLPHOSPHORIMIDATES

M. I. Kabachnik and V. A. Gilyarov

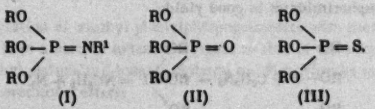
In a previous paper [1], which was devoted to the synthesis and the investigation of the properties of dialkyl phenylphosphoramidates, we described the alkylation of the sodium derivative of a dialkyl phenylphosphoramidate with an alkyl halide, which resulted in the formation of a P-alkyl-N-phenylphosphonimidic ester:



A substance of the same structure was synthesized also by the action of phenyl azide on an alkylphosphonous ester:

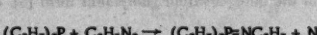


The products were the first P-alkylphosphonimidic acid derivatives to be prepared. The corresponding trialkyl phosphorimidates (I) are the nitrogen analogs of trialkyl phosphates (II) and trialkyl phosphorothionates (III):

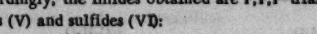


Whereas the last two classes of substances have been known for a long time and have been thoroughly studied, trialkyl phosphorimidates have not been described previously.

Organic derivatives of quinquevalent phosphorus containing the grouping P=N were described by Staudinger and coworkers [2], who prepared them by the action of phenyl azide on trialkylphosphines:



Horner and Gross [3] recently studied this reaction in detail and applied it to various azides. However, apart from our synthesis referred to above, Staudinger's reaction has been applied to phosphines, and not to esters of tervalent phosphorus acids. Accordingly, the imides obtained are P,P,P-triarylphosphine imides (IV), the nitrogen analogs of triarylphosphine oxides (V) and sulfides (VI):



As Staudinger and coworkers showed, phosphine amides have many very interesting properties. Even more interesting properties are to be expected from imido derivatives of phosphoric and phosphonic esters of type (I), which contain the $p\pi$-conjugated system of bonds $R-O-\underset{\underset{|}{}}{P}=N-$. Substances of a closely related type were systematically investigated by Kirsanov and coworkers [4]. By reaction of phosphorus pentachloride with amides of carboxylic or sulfonic acids they obtained N-acyl-P,P,P-trichlorophosphine imides:

$$Ac{\cdot}NH_2 + PCl_5 = 2HCl + Ac{\cdot}N{=}PCl_3$$

which were converted into various derivatives by the action of alcohols and other reagents. However, Kirsanov's compounds contained an acyl group on nitrogen, i. e., were the mixed imides of two acids, namely, phosphoric acid and a carboxylic or sulfonic acid. It would appear that the preparation of substances of type (I) by Kirsanov's method is impossible.

TABLE

No.	Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
1	$(CH_3O)_3P{=}NC_6H_5$	44-45 ($2\cdot10^{-4}$)	1.5232	1.1713
2	$(C_2H_5O)_3P{=}NC_6H_5$	118-119 (1.5)	1.5022	1.0743
3	$(C_3H_7O)_3P{=}NC_6H_5$	122 (1)	1.4920	1.0297
4	$(i\text{-}C_3H_7O)_3P{=}NC_6H_5$	49-50 ($2\cdot10^{-4}$)	1.4880	1.0116
5	$(C_4H_9O)_3P{=}NC_6H_5$	144-145 (1)	1.4885	1.0036
		91-92 (1)	1.5030	1.1233
6	$(C_2H_5O)_2P(O)N(CH_3)C_6H_5$	99 (1.5)	1.5030	1.1237
7	$(C_2H_5O)_2P(O)N(C_2H_5)C_6H_5$	91 (0.5)	1.4972	1.0917
8	$(C_2H_5O)_2P(O)N(COCH_3)C_6H_5$	84-84.5 (0.01)	1.5038	1.1670

We investigated the reaction of phenyl azide with trialkyl phosphites and found it proceeded smoothly with formation of trialkyl phenylphosphorimidates in good yield:

$$(RO)_3P + C_6H_5N_3 \rightarrow (RO)_3P{=}NC_6H_5 + N_2.$$

Constants of the substances obtained (Nos. 1-5) are given in the table*.

Esters of quinquevalent phosphorus acids (trialkyl phosphates, dialkyl phenylphosphoramidates), as also dialkyl hydrogen phosphites and O,O-dialkyl hydrogen phosphorothioites, the tautomeric equilibrium of which is greatly displaced in the direction of the quinquevalent phosphorus form [5], do not react with phenyl azide. We

* It must be mentioned that, in the case of triisopropyl phosphite, it is necessary to distill the reaction products in a high vacuum. Otherwise, the main reaction product is diisopropyl phenylphosphoramidate, formed, probably, by the pyrolysis of triisopropyl phenylphosphorimidate:

$$(i\text{-}C_3H_7O)_3P{=}NC_6H_5 \rightarrow C_3H_6 + (i\text{-}C_3H_7O)_2P(O)NHC_6H_5.$$

therefore consider that reaction with phenyl azide can be regarded as characteristic of tervalent phosphorus compounds. Like the well known Arbuzov rearrangement [5], addition of sulfur [6], and addition of a cuprous halide [5], reaction with phenyl azide may be useful for the investigation of the structures of certain organophosphorus compounds.

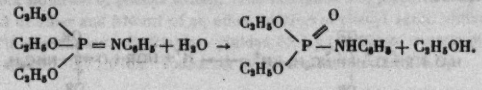
An investigation of the properties of trialkyl phenylphosphorimidates gave interesting results. In some reactions they behave like Staudinger's phosphine imides: thus, when treated with carbon disulfide they exchange the phenylimido group for a sulfur atom, and phenyl isothiocyanate is formed simultaneously:

$$(RO)_3P{=}NC_6H_5 + CS_2 \rightarrow (RO)_3P{=}S + C_6H_5N{=}C{=}S.$$

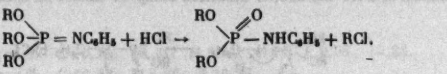
In some reactions, however, not only the P=N linkage has a specific effect on the course of the process, but also the presence of alkoxy groups attached to phosphorus. Thus, it was found that the product of the hydrolysis of triethyl phenylphosphorimidate was not triethyl phosphate, as might be expected on analogy with the reaction of phosphine imides:

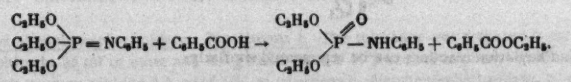
$$Ar_3P{=}NC_6H_5 + H_2O \rightarrow Ar_3PO + C_6H_5NH_2,$$

but diethyl phenylphosphoramidate:



An analogous result was obtained in reactions with anhydrous hydrogen chloride and with benzoic acid in an inert medium:

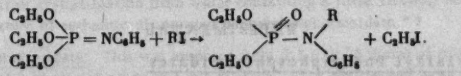




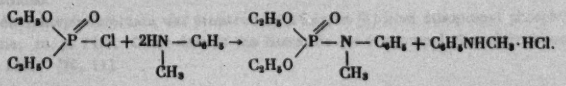
Investigation of the alkylation of triethyl phenylphosphorimidate with methyl iodide showed that this reaction proceeds in a way that is to a certain extent analogous to that of the alkylation of trialkyl phosphorothionates. As is well known, trialkyl phosphorothionates undergo the Pishchimuka rearrangement [7] with alkyl halides with formation of phosphorothiolic esters:

$$(RO)_3PS + R'I \rightarrow (RO)_2PO(SR') + RI.$$

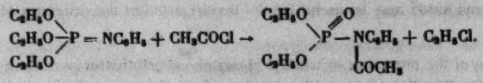
Correspondingly, triethyl phenylphosphorimidate reacts with alkyl halides with formation of diethyl alkylphenylphosphoramidates:



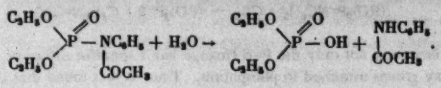
We proved the structure of the rearrangement product obtained by the action of methyl iodide by confirmatory synthesis from diethyl phosphorochloridate and N-methylaniline:



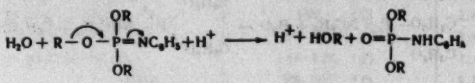
Reaction with acetyl chloride is analogous to the methylation reaction, the acetyl derivative of the phenylphosphoramidic ester being formed:



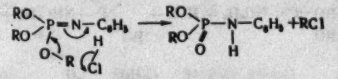
The structure of the product was proved by the formation of acetanilide by hydrolysis:



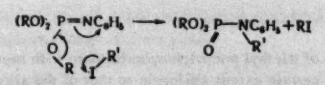
It may be considered that the reactions of trialkyl phenylphosphorimidates with water, with hydrogen chloride, and with benzoic acid are extremely similar in type. In all three cases the action of the reagent is directed to the 1,4-positions of the $\sigma\pi$-conjugated system R—O—P=N—, and reaction proceeds with transfer of reaction center. For the hydrolysis reaction, which proceeds in a conducting medium, a scheme that is usual for reactions of this kind may be proposed:



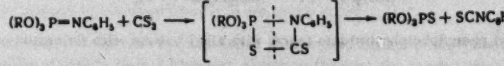
However, for the action of hydrogen chloride in an isooctane medium or of benzoic acid in a xylene medium, reaction with formation of a six-membered transition complex cannot be excluded:



Alkylation and acylation reactions can be represented similarly:



Unlike these reactions, the reaction of carbon disulfide proceeds only at the P=N bond and is therefore directed to the 1,2-positions:



EXPERIMENTAL

Preparation of Trialkyl Phenylphosphorimidates

An ether solution of phenyl azide was added dropwise to a stirred ether solution of the trialkyl phosphite, the reaction mixture being cooled with ice. Evolution of nitrogen was observed 3-5 minutes after the addition was begun. The mixture was set aside for 30 minutes at room temperature, ether was distilled off, and the residue was vacuum distilled.

Trimethyl phenylphosphorimidate. This was prepared from 8.7 g (0.07 mole) of trimethyl phosphite in 25 ml of ether and 10.7 g (0.09 mole) of phenyl azide in 7 ml of ether. Two distillations in high vacuum gave 12.0 g (80.0%) of trimethyl phenylphosphorimidate, b. p. 44-45° ($1 \cdot 10^{-4}$ mm); n_D^{20} 1.5232; d_4^{20} 1.1713; found MR 56.10; calculated MR 56.82*.

Found %: C 50.58, 50.65; H 6.50, 6.73; P 14.03, 14.15.
$C_9H_{14}O_3NP$. Calculated %: C 50.23; H 6.51; P 14.43.

The product is a colorless liquid, soluble in ether and alcohol, insoluble in water and isooctane.

Triethyl phenylphosphorimidate. Experiment 1. The substance was prepared from 16.6 g (0.1 mole) of triethyl phosphite in 50 ml of ether and 11.9 g (0.1 mole) of phenyl azide in 20 ml of ether. Three successive fractionations yielded 16.3 g (63.0%) of triethyl phenylphosphorimidate, b. p. 135° (3.5 mm) and 118-119° (1.5 mm); n_D^{20} 1.5022; d_4^{20} 1.0743; found MR 70.66; calculated MR 70.67.

Found %: C 55.68, 55.66; H 7.85, 7.83; P 12.00, 12.15.
$C_{12}H_{20}O_3NP$. Calculated %: C 56.04; H 7.78; P 12.08.

The product is a brownish liquid, soluble in organic solvents, insoluble in water.

Experiment 2 (without isolation of phenyl azide). The substance was prepared from 41.5 g (0.25 mole) of triethyl phosphite in 50 ml of ether and 270 ml of an ether solution of phenyl azide which contained 35.7 g (0.3 mole) of phenyl azide. Three successive distillations yielded 55.2 g (86.2%) of triethyl phenylphosphorimidate, b. p. 100° (0.8 mm); n_D^{20} 1.5038; d_4^{20} 1.0752; found MR 70.79; calculated MR 70.67.

Tripropyl phenylphosphorimidate. This was prepared from 8.3 g (0.04 mole) of tripropyl phosphite in 25 ml of ether and 4.8 g (0.04 mole) of phenyl azide in 5 ml of ether. Two distillations gave 7.5 g (62.8%) of tripropyl phenylphosphorimidate, b. p. 122° (1 mm); n_D^{20} 1.4920; d_4^{20} 1.0297; found MR 84.30; calculated MR 84.52.

Found %: C 60.14, 60.41; H 8.81, 8.54; P 9.98, 10.23.
$C_{15}H_{26}O_3NP$. Calculated %: C 60.16; H 8.69; P 10.36.

Triisopropyl phenylphosphorimidate. Experiment 1. The substance was prepared from 6.3 g (0.03 mole) of triisopropyl phosphite in 25 ml of ether and 4.0 g (0.03 mole + 10% excess) of phenyl azide in 5 ml of ether. Two distillations in high vacuum yielded 5.6 g (64.3%) of triisopropyl phenylphosphorimidate, b. p. 49-50° ($2 \cdot 10^{-4}$ mm); n_D^{20} 1.4880; d_4^{20} 1.0116; found MR 85.21; calculated MR 84.52.

Found %: C 59.96, 59.82; H 8.52, 8.67; P 10.74, 10.53.
$C_{15}H_{26}O_3NP$. Calculated %: C 60.16; H 8.69; P 10.36.

The product is a yellowish liquid.

Experiment 2. Reaction was between 7.6 g (0.037 mole) of triisopropyl phosphite in 25 ml of ether and 5.3 g (0.045 mole) of phenyl azide in 5 ml of ether, and the first distillation gave a fraction (5.7 g) having b. p. 114-116° (1.5 mm) and n_D^{20} 1.4479; which we were unable to distill a second time (bath temperature up to 205°, p = 1.5 mm). When cool, the substance crystallized, and the crystals were pressed off on a porous plate (3.4 g of crystals, m. p. 117.5-118°). After crystallization from water containing a little alcohol, the crystals had m. p. 118.5-119°, undepressed by admixture of authentic diisopropyl phenylphosphoramidate.**

Tributyl phenylphosphorimidate. This was prepared from 7.5 g (0.03 mole) of tributyl phosphite in 25 ml of ether and 3.6 g (0.03 mole) of phenyl azide in 5 ml of ether. Two distillations gave 7.1 g (69.0%) of tributyl phenylphosphorimidate, b. p. 114-145° (1 mm); n_D^{20} 1.4885; d_4^{20} 1.0036; found MR 98.06; calculated MR 98.37.

* The atomic refraction of nitrogen was taken to be 5.78 (calculated from data obtained in the present and preceding [1] investigations).

** Diisopropyl phenylphosphoramidate was prepared by Atherton [8] from diisopropyl phosphite, bromotrichloromethane, and aniline; m. p. 119°. Other data in the literature for diisopropyl phenylphosphoramidate are: m. p. 120-121° [9]; 121-121.5° [10, 11].

Properties of Trialkyl Phenylphosphorimidates

Action of carbon disulfide on triethyl phenylphosphorimidate. When 6.8 g (0.09 mole) of carbon disulfide was added to 7.7 g (0.03 mole) of triethyl phenylphosphorimidate, no changes were observed. The solution was refluxed at 60-65° for six hours. Carbon disulfide was distilled off under reduced pressure, residual traces being removed by treatment for one hour at 50° and 15 mm pressure. The product, which had the odor of phenyl isothiocyanate, was treated with 2.8 g (0.03 mole) of aniline. The mixture, which crystallized out, was heated for 90 minutes at 65-70° in order to complete the reaction. The precipitate was separated and washed with ether (four 10-ml portions). The precipitate weighed 4.7 g (68.5%), m. p. 147.5°. After recrystallization from alcohol it melted at 151°. Melting point of a mixture with 1,3-diphenyl-2-thiourea was 151°. The ether extract was washed with two 10-ml portions of 10% sulfuric acid and then with water until the reaction was neutral. The ether solution was dried with calcined sodium sulfate, ether was distilled off under reduced pressure, and the residue was distilled. Two distillations yielded 4.2 g (47%) of O,O,O-triethyl phosphorothioate, b. p. 82° (7 mm); n_D^{20} 1.4550; d_4^{20} 1.0746; d_0^{20} 1.0733; found MR 49.99; calculated on $C_8H_{15}O_3PS$ MR 49.39. For O,O,O-triethyl phosphorothioate, the literature [12] gives b. p. 88.5° (8 mm); n_D^{20} 1.4480; d_0^{20} 1.0756.

A complex was prepared from 0.5 g (0.025 mole) of the triethyl phosphorothioate and 2.2 g (0.05 mole) of mercuric chloride by Pishchimuka's method [7]; it melted at 101-102° (from alcohol). A mixture with the complex prepared from authentic O,O,O-triethyl phosphorothioate melted at 100-101°. For a complex of composition $(C_2H_5O)_3P{=}S \cdot 2HgI_2$, the literature [7] gives m. p. 88°.

Hydrolysis of triethyl phenylphosphorimidate. When 10 ml of water was added to 2 g of triethyl phenylphosphorimidate, no reaction was observed. When the mixture had stood for 1.5 months, the oily layer crystallized. The crystals were separated and dried in a vacuum desiccator over phosphoric oxide. The product was 1.47 g (83%) of diethyl phenylphosphoramidate, m. p. 94-95°, unchanged by recrystallization from isooctane. A mixture with known diethyl phenylphosphoramidate melted at 94-95°. The literature gives melting points from 93° [13] to 96.5° [10].

Action of benzoic acid on triethyl phenylphosphorimidate. When 1.3 g (0.05 mole) of triethyl phenylphosphorimidate was added to a mixture of 0.6 g (0.05 mole) of benzoic acid and 5 ml of dry xylene, a homogeneous solution was formed and the odor of ethyl benzoate was noted. In order to complete reaction the mixture was heated at 90° for three hours. When solvent was removed under reduced pressure, the residue (a yellow liquid) crystallized. The crystals were washed with isooctane and dried in a vacuum desiccator. The yield of diethyl phenylphosphoramidate was 0.87 g (77%). It had m. p. 92.5-93°, raised to 94-95° by recrystallization from isooctane. A mixture with known diethyl phenylphosphoramidate melted at 94-95°.

Action of hydrogen chloride on triethyl phenylphosphorimidate. When dry hydrogen chloride is passed through a solution of 1.2 g triethyl phenylphosphorimidate in 5 ml isooctane (cooling with water) absorption of hydrogen chloride and formation of a white precipitate is observed. Passage of hydrogen chloride was continued for three minutes after absorption had ceased. After additional treatment with hydrogen chloride the solution was distilled in vacuum; the residue (crystals) was washed in isooctane and dried in a vacuum desiccator. Yield 0.975 g diethyl phenylphosphoramidate (96%); m. p. 93.5-94°. After recrystallization from isooctane it had m. p. 95°. A mixture with known diethyl phosphoramidate melted at 95°.

Action of hydrogen chloride on trimethyl phenylphosphorimidate. Dry hydrogen chloride was passed for ten minutes through 1 g of trimethyl phenylphosphorimidate under a layer of 5 ml of isooctane, the system being cooled with cold water. Hydrogen chloride and isooctane were distilled off under reduced pressure, and the residue (a very viscous mass) was pressed off on a porous plate (weight 0.75 g). After recrystallization from isooctane, 0.55 g (48%) of dimethyl phenylphosphoramidate was obtained; m. p. 88°. For dimethyl phenylphosphoramidate the literature [11] gives m. p. 88-88.5°.

Reaction of alkyl halides with triethyl phenylphosphorimidate. a) When 3.8 g (0.015 mole) of triethyl phenylphosphorimidate was mixed with 9.3 (0.06 mole) of ethyl iodide, no change was observed. After four days ethyl iodide was distilled off under reduced pressure and the residue was distilled. The product (3.5 g) was unchanged triethyl phenylphosphorimidate, b. p. 89° (0.5-0.6 mm), n_D^{20} 1.5025; d_4^{20} 1.0789.

b) A mixture of 5.1 g (0.02 mole) of triethyl phenylphosphorimidate and 11.3 g (0.08 mole) of methyl iodide was heated fro seven hours at 65-75° in a flask having a reflux condenser fitted with a calcium chloride tube. Methyl iodide was distilled off under reduced pressure, and distillation of the residue gave 4.4 g (90.5%) of diethyl methyl-

phenylphosphoramidate, b. p. 91-92° (1 mm); n_D^{20} 1.5030; d_4^{20} 1.1233; found MR 63.98.

Found %: C 54.14, 54.30; H 7.72, 7.61; P 12.59, 12.59.
$C_{11}H_{18}O_3NP$. Calculated %: C 54.32; H 7.41; P 12.76.

c) A mixture of 5.1 g (0.02 mole) of tritheyl phenylphosphorimidate and 11.3 g (0.08 mole) of methyl iodide was heated in a sealed tube for four hours at 100°. The yield of diethyl methylphenylphosphoramidate was 4.4 g (90.5%); b. p. 101° (1.5 mm); n_D^{20} 1.5030; d_4^{20} 1.1233.

d) A mixture of 3.8 g (0.015 mole) of triethyl phenylphosphorimidate and 9.3 g (0.06 mole) of ethyl iodide was refluxed at 65-70° for six hours. Ethyl iodide was distilled off under reduced pressure. Distillation of the residue gave 3.5 g (92%) of diethyl ethylphenylphosphoramidate, b. p. 91° (0.5 mm); n_D^{20} 1.4972; d_4^{20} 1.0917; found MR 68.94.

Found %: C 56.03, 56.23; H 7.90, 8.00; P 11.99, 12.07.
$C_{12}H_{20}O_3NP$. Calculated %: C 56.04; H 7.78; P 12.08.

Preparation of diethyl methylphenylphosphoramidate. N-Methylaniline (12.2 g, i. e., 0.14 mole) was added dropwise to 10.0 g (0.057 mole) of diethyl phosphorochloridate in 50 ml of ether contained in a three-necked flask fitted with stirrer, dropping funnel, and condenser. After a few minutes a crystalline precipitate began to form and gradually increased in quantity. After one day the precipitate was separated and washed with ether. The weight of methylaniline hydrochloride was 7.5 g (theory requires 8.2 g). Two successive distillations gave 5.5 g (40%) of dimethyl methylphenylphosphoramidate, b. p. 99° (1.5 mm), n_D^{20} 1.5030; d_4^{20} 1.1237.

Found %: C 54.03, 54.27; H 7.54, 7.67; P 12.59, 12.32.
$C_{11}H_{18}O_3NP$. Calculated %: C 54.32; H 7.41; P 12.76.

Action of acetyl chloride on triethyl phenylphosphorimidate. Acetyl chloride (3.1 g, i. e., 0.04 mole) was added dropwise to a solution of 10.3 g (0.04 mole) of triethyl phenylphosphorimidate in 2.5 ml of isooctane. When addition was complete, the solution was heated to 58°, when it became turbid. The mixture was heated under reflux for three hours at 70°. The lower, oily layer was separated and washed with 20 ml of isooctane. Traces of solvent were removed at 2 mm from a boiling water bath. The residue, a thick brown liquid, weighed 9.4 g. Distillation gave 7.4 g (68.2%) of diethyl acetylphenylphosphoramidate, b. p. 84-84.5° (0.01 mm); n_D^{20} 1.5038; d_4^{20} 1.1670; found MR 68.7.

Found %: P 11.41, 11.56.
$C_{12}H_{18}O_4NP$. Calculated %: P 11.44.

Hydrolysis of diethyl acetylphenylphosphoramidate. A mixture of 0.8 g of diethyl acetylphenylphosphoramidate and 8 ml of water was heated for three hours in a boiling water bath. Cooling resulted in the formation of 0.14 g of a crystalline precipitate, m. p. 113-114°, undepressed by admixture of acetanilide. The yield of acetanilide was 30%.

SUMMARY

1. Trialkyl phenylphosphorimidates $(RO)_3P{=}NC_6H_5$ were synthesized by reaction of trialkyl phosphites with phenyl azide.

2. Some properties of trialkyl phenylphosphorimidates were studied. It was shown that reaction of triethyl penylphosphorimidate with water, hydrogen chloride, or benzoic acid gave diethyl phenylphosphoramidate. Reaction of triethyl phenylphosphorimidate with alkyl halides gave diethyl alkylphenylphosphoramidates, and reaction with acetyl chloride gave diethyl acetylphenylphosphoramidate.

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POLYORGANOSTANNO- AND POLYORGANOTITANOSILOXANES

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In 1947 one of us showed that organosilicon compounds containining silico-attached hydroxyls react with metals and their hydroxides with formation of macromolecular compounds containing metallosiloxane groups [1]. We later synthesized nonaethylaluminoxytrisiloxane and established its structure [2]. Further investigations showed that polyorganometallosiloxanes were obtained also by an exchange reaction between the hydrolysis products of organosilicon monomers and salts of multivalent metals and by cohydrolysis of organosilicon monomers with salts of multivalent metals [3]. In the present paper we describe some new polymers: polyorganostanno- and polyorganotitanosiloxanes.

a) Polyorganostannosiloxanes. Glassy polyorganostannosiloxanes were prepared by the cohydrolysis of diethyltin dichloride with dichlorodiethylsilane and also with a mixture of dichlorodiethylsilane and trichlorophenylsilane with subsequent condensation of the cohydrolysis products. Investigation of the fractional composition of the polymer obtained from 0.6 mole of dichlorodiethylsilane, 0.3 mole of trichlorophenylsilane, and 0.1 mole of diethyltin dichloride showed that all fractions contained both silicon and tin, but the relative amounts varied: the alcohol-soluble fraction contained more tin than the acetone- and toluene-soluble fractions (Table 1).

TABLE 1

Substance	Amount (g)	Content (%)		Si : Sn ratio
		of silicon	of tin	
Polymer No. 4	8.6193	20.79	8.60	10.3 : 1
Alcohol fraction	0.6192	17.34	17.86	4.1 : 1
Acetone fraction	2.4127	21.18	9.69	9.3 : 1
Toluene fraction	4.5884	22.61	8.60	11.5 : 1
Losses	0.9890	–	–	–

The experimental results showed that the cohydrolysis of alkyl- or aryl-chlorosilanes with diethyltin dichloride resulted in the formation of glassy polyorganostannosiloxanes in accordance with the scheme:

$$R_2SiCl_2 + (C_2H_5)_2SnCl_2 \xrightarrow[NH_3]{H_2O} (-OR_2Si-)_m-O-\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\underset{|}{\overset{|}{Sn}}}}-O-,$$

in which m, as the experimental results show, varies from 4 to 11. The compositions of the polyorganostannosiloxanes vary according to the relative amounts of the monomers taken for reaction. Moreover, fractionation showed that a given polymer contains various fractions, in which the Si : Sn ratio varies from 4 to 11.

b) Polyorganotitanosiloxanes. By the cohydrolysis of alkyl- or aryl-chlorosilanes with tetrabutyl orthotitanate and by reaction of the hydrolysis products of alkyl- or aryl-chlorosilanes with tetrabutyl orthotitanate and subsequent condensation at 200°, glassy polymers are obtained which are soluble in organic solvents. For example, cohydrolysis of 0.66 mole of dichlorodimethylsilane, 0.33 mole of trichlorophenylsilane, and 0.1 mole of tetrabutyl orthotitanate gave an alcohol- and acetone-soluble polymer. Fractionation of this polymer showed that all

fractions contain both silicon and titanium (Table 2).

TABLE 2

Substance	Amount (g)	Content (%)		Si : Ti ratio
		of silicon	of titanium	
Polymer No. 5	6.3522	24.91	1.47	29.6 : 1
Alcohol fraction	1.8396	27.43	1.17	40.7 : 1
Acetone fraction	3.6028	26.46	1.84	24.8 : 1
Toluene fraction	0.4010	Not analyzed		
Losses	0.5088	–	–	–

Cohydrolysis of 0.66 mole of dichlorodiethylsilane, 0.33 mole of trichlorophenylsilane, and 0.1 mole of tetrabutyl orthosilicate gave an alcohol- and acetone-soluble polymer. Investigation of the fractional composition of this polymer showed that all fractions contain both silicon and titanium (Table 3).

TABLE 3

Substance	Amount (g)	Content (%)		Si : Ti ratio
		of silicon	of titanium	
Polymer No. 4	10.080	23.54	1.83	23.22 : 1
Alcohol fraction	0.797	23.22	1.62	24.51 : 1
Acetone fraction	8.930	23.99	2.25	18.23 : 1
Toluene fraction	0.205		Not analyzed	
Losses	0.148	–	–	–

The experimental results show that the organosilicon monomers react with tetrabutyl orthotitanate in accordance with the scheme:

$$R_2SiCl_2 + Ti(OC_4H_9)_4 \xrightarrow[NaOH]{H_2O} (-OR_2Si-)_m-O-\underset{\displaystyle OC_4H_9}{\overset{\displaystyle OC_4H_9}{\underset{|}{\overset{|}{Ti}}}}-O-$$

Table 4 gives the compositions of fractions of the polymer obtained by reaction of the cohydrolysis products from 0.66 mole of dichlorodimethylsilane and 0.33 mole of trichlorophenylsilane with 0.1 mole of tetrabutyl orthotitanate and subsequent condensation at 200°. All fractions contain both silicon and titanium, and the silicon-titanium ratio varies: acetone-soluble fractions contain considerably more titanium than alcohol-soluble fractions. Here, as in the case of polyorganostannosiloxanes, the relative amounts of silicon and metal in the polymers varies according to the monomer ratio in the mixture taken for reaction. Fractionation of polyorganotitanosiloxanes prepared by various methods showed that a polymer of given overall composition contains various fractions. For example, Polymer No. 8 (Table 4) contains an alcohol-soluble fraction having a Si : Ti ratio of 30 : 1 and an acetone-soluble fraction having a Si : Ti ratio of 5 : 1. The experimental results, therefore, show that m varies from 5 to 30.

EXPERIMENTAL

Substances used were: dichlorodimethylsilane of chlorine content 55.2% (calculated 54.98% Cl), dichlorodiethylsilane of chlorine content 44.5% (calculated 45.18% Cl), trichlorophenylsilane of chlorine content 50.1% (calculated 50.31% Cl). Diethyltin dichloride, m. p. 84°, was prepared by Kocheshkov's method [4]. Tetrabutyl orthotitanate, b. p. 200-202° (26 mm), was prepared by Nesmeyanov's method [5].

TABLE 4

Substance	Amount (g)	Content (%) of silicon	Content (%) of titanium	Si : Ti ratio
Polymer No. 8	6.1502	22.30	6.11	6.3 : 1
Alcohol fraction	1.0894	22.90	1.29	30.3 : 1
Acetone fraction	4.3830	22.87	7.40	5.3 : 1
Toluene fraction	0.1464		Not analyzed	
Losses	0.5314	–	–	–

Synthesis of Polyorganostannosiloxanes by Cohydrolysis of Alkyl- and Aryl-chlorosilanes with Diethyltin Dichloride

The reaction was carried out in a three-necked flask fitted with mercury-sealed stirrer, thermometer, dropping funnel, and reflux condenser. The calculated amounts of 10% aqueous ammonia and toluene were introduced into the flask, heated to 50-55°, and stirred while a mixture of a toluene solution of diethyltin dichloride and the alkyl- or aryl-chlorosilane was added over a period of one hour. During the cohydrolysis, the mixture was kept alkaline (final pH 8.5). When reaction was complete, the toluene layer was separated and washed with water; toluene was distilled off under reduced pressure (20 mm; temperature 35°). Clear yellow liquid polymers were obtained; they were soluble in benzene, toluene, ether, acetone, and alcohol; when heated, they passed into a infusible, insoluble state. The yields of hydrolysis products and the analytical results are given in Table 5.

TABLE 5

Experiment No.	Amounts of reactants (moles): Dichlorodimethylsilane	Dichlorodiethylsilane	Trichlorophenylsilane	diethyltin dichloride	Yield of liquid polymer (g)	Content (%) of HO	Si	Sn	Si : Sn ratio
1	0.5	—	—	0.1	105,0	0.19	7.21	5.19	5.9 : 1
2	0.9	—	—	0.1	89,4	0.27	17.91	3.39	22.5 : 1
3	—	0.9	—	0.1	78,0	—	23.33	6.50	15.2 : 1
4	—	0.6	0.3	0.1	75,0	—	22.08	7.87	11.9 : 1

The liquid hydrolysis products were condensed to solid polymers at 105-150°. The analytical results on the condensation products so obtained are given in Table 6.

TABLE 6

Experiment No.	Amounts of reactants (moles): Dichlorodimethylsilane	Dichlorodiethylsilane	Trichlorophenylsilane	Diethyltin dichloride	Tin content of liquid polymer (%)	Content in polymer of: Silicon (%)	Tin (%)	Si : Sn ratio
1	0.5	—	—	0.1	5.19	24.53	16.58	6.3 : 1
2	0.9	—	—	0.1	3.39	29.90	4.87	26 : 1
3	—	0.9	—	0.1	6.50	24.63	5.85	17.9 : 1
4	—	0.6	0.3	0.1	7.87	20.79	8.60	10.3 : 1

Investigation of Polyorganostannosiloxanes

The polymer under investigation (0.2-0.3 g) and concentrated sulfuric acid (20 ml) were introduced into a glass beaker. When the polymer had dissolved, 2 g of potassium iodate was added, and the contents of the beaker were gradually heated until iodine vapor ceased to be evolved and the solution cleared. The excess of sulfuric acid was then evaporated off, and 50 ml of distilled water and 50 ml of dilute (3:2) hydrochloric acid were added. The resulting solution was diluted with distilled water to 400 ml. When the solution was boiled, a precipitate of silica was formed, which was filtered off through an ashless filter paper and washed with hot 5% hydrochloric acid and with water. The filter paper and precipitate were burnt and calcined, and the silicon was determined. The calculation was by the formula:

$$\text{silicon (\%)} = \frac{(\text{weight of ppt.}) \cdot 0.4672 \cdot 100}{(\text{weight of sample})}$$

To separate the tin the filtrate was evaporated down to 200 ml and neutralized with ammonia. Ammonium nitrate (25 g) was added, and the total volume was made up to 300 ml. The mixture was boiled, and the precipitate that formed was filtered off and washed with hot 2% ammonium nitrate solution. The filter paper and precipitate were burnt in an oxidizing flame. The tin content was calculated from the formula:

$$\text{tin (\%)} = \frac{(\text{weight of ppt.}) \cdot 0.7876 \cdot 100}{(\text{weight of sample})}$$

The results obtained are given in Tables 5 and 6.

Synthesis of Polyorganotitanosiloxanes

a) Cohydrolysis of alkyl- and aryl-chlorosilanes with tetrabutyl orthosilicate. A mixture of 10% caustic soda solution and toluene was prepared in a glass vessel fitted with stirrer, thermometer, and dropping funnel. The mixture was stirred, and a mixture of alkyl(aryl)chlorosilane and tetrabutyl orthotitanate was added from the dropping funnel over a period of 60-90 minutes at 20-22°. When hydrolysis was complete, the reaction mixture was a liquid containing a precipitate which was filtered off; the toluene layer of the filtrate was separated from water and washed, and toluene was distilled off under reduced pressure. Clear, light-yellow, liquid polymers were obtained. They were soluble in ether, benzene, toluene, alcohol, and acetone. When heated, they passed into a solid, infusible state. The yields of products and the results of their analysis are given in Table 7.

TABLE 7

Experiment No.	Amounts of reactants (moles)				Yield of liquid polymer (g)	Content (%) of		Si:Ti ratio
	Dichlorodimethylsilane	Dichlorodiethylsilane	Trichlorophenylsilane	Tetrabutyl orthotitanate		Si	Ti	
1	—	—	1.0	0.1	7.0	23.1	1.44	27.5 : 1
2	—	1.0	—	0.1	3.5	23.4	1.63	24.6 : 1
3	1.0	—	—	0.1	3.5	31.5	0.78	69 : 1
4	—	0.66	0.33	0.1	79.8	22.50	1.62	23.5 : 1
5	0.66	—	0.33	0.1	58	22.15	2.72	13.6 : 1

When the liquid polymers were heated to 200°, glassy products were obtained which were soluble in organic solvents. The results of the analysis of the condensation products are given in Table 8.

b) Reaction of hydrolysis products of alkyl- and aryl-chlorosilanes with tetrabutyl orthotitanate. The reaction was carried out in two stages: 1) hydrolysis of the alkyl(aryl)chlorosilanes, and 2) heating of the hydrolysis products with tetrabutyl orthotitanate. Water, the calculated amount of sodium carbonate, and toluene were introduced into the hydrolysis vessel. The contents of the vessel were stirred at 20-22° while the mixture of alkyl-(aryl)chlorosilanes was added from a dropping funnel over a period of one hour. The toluene layer was washed,

TABLE 8

Experiment No.	Amounts of reactants (moles)				Titanium content of liquid polymer (%)	Content (%) in condensation product of		Si : Ti ratio
	Dichlorodimethylsilane	Dichlorodiethylsilane	Trichlorophenylsilane	Tetrabutyl orthotitanate		Si	Ti	
4	—	0.66	0.33	0.1	1.62	23.54	1.83	21.96 : 1
5	0.66	—	0.33	0.1	2.79	24.91	1.47	20.96 : 1

carefully separated from water, and transferred to a three-necked flask fitted with stirrer, thermometer, reflux condenser, and dropping funnel. The solution was stirred at 20°, and a 50% toluene solution of tetrabutyl orthotitanate was added from the dropping funnel over a period of one hour. The reaction mixture was then heated at 80-85° for 4-5 hours, after which toluene was distilled off under reduced pressure. Liquid polymers were obtained; they were soluble in ether, benzene, toluene, alcohol, and acetone. The yields of products and the results of their analysis are given in Table 9.

The liquid polymers were condensed by heating them at 200°. The products were glassy substances, soluble in organic solvents. Results of the analysis of the condensation products are given in Table 10.

TABLE 9

Experiment No.	Amounts of reactants (moles)				Yield of liquid polymer (g)	Content (%) of		Si : Ti ratio
	Dichlorodimethylsilane	Dichlorodiethylsilane	Trichlorophenylsilane	Tetrabutyl orthotitanate		Si	Ti	
6	1.0	—	—	0.1	22.5	27.41	2.07	22.7 : 1
7	—	1.0	—	0.1	125.0	21.03	6.59	5.5 : 1
8	0.66	—	0.33	0.1	63.0	22.17	5.99	6.4 : 1
9	—	0.66	0.33	0.1	80.0	19.40	5.80	5.7 : 1

TABLE 10

Experiment No.	Amounts of reactants (moles)				Titanium content of liquid polymer (%)	Content (%) in condensation product of		Si : Ti ratio
	Dichlorodimethylsilane	Dichlorodiethylsilane	Trichlorophenylsilane	Tetrabutyl orthotitanate		Si	Ti	
8	0.66	—	0.33	0.1	5.99	22.30	6.11	6.22 : 1
9	—	0.66	0.33	0.1	5.80	20.34	6.24	5.47 : 1

Investigation of Polyorganotitanosiloxanes

The investigation of the polyorganotitanosiloxanes was carried out by the procedure described for polyorganostannosiloxanes. The filtrate after the precipitation of silica was rendered neutral with ammonia, and 2 g of ammonium chloride was added. The precipitate that formed was filtered off and washed with 2% ammonium chlo-

ride solution. The filter paper and precipitate were burnt and calcined; the ash was weighed. The calculation was carried out by the formula:

$$\text{titanium (\%)} = \frac{\text{(weight of ppt.)} \cdot 0.5994 \cdot 100}{\text{(weight of sample)}}$$

The results obtained are given in Tables 7, 8, 9, and 10.

SUMMARY

1. The syntheses were effected of new polymeric substances, i. e., polyorganostannosiloxanes and polyorganotitanosiloxanes, the chains of which contain not only siloxane links $-\overset{\diagdown\diagup}{\underset{\diagup\diagdown}{Si}}-O-\overset{\diagdown\diagup}{\underset{\diagup\diagdown}{Si}}-$, but also $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-\overset{\diagdown}{\underset{\diagup}{Sn}}-$ and $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-\overset{\diagdown}{\underset{\diagup}{Ti}}-$ links.

2. It was shown that $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-\overset{\diagdown}{\underset{\diagup}{Sn}}-$ and $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-\overset{\diagdown}{\underset{\diagup}{Ti}}-$ links in polyorganostanno- and polyorganotitanosiloxanes are broken down by strong sulfuric acid.

3. It was found that polyorganostanno- and polyorganotitanosiloxanes are soluble in organic solvents. The fractional compositions of these products were studied, and it was shown that they are cocondensation products.

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REACTION OF TRIALKYLSILANES WITH IODINE AND HYDROGEN IODIDE

M. G. Voronkov and Yu. I. Khudobin

The simplest and most convenient methods for the synthesis of trialkyliodosilanes R_3SiI are reaction of hexaalkyldisiloxanes with aluminum iodide [1] or aluminum and iodine [2] and reaction of trialkylsilanes with elementary iodine [3-6]*. The literature [3-6] indicates that the latter reaction proceeds in accordance with the equation:

$$R_3SiH + I_2 \longrightarrow R_3SiI + HI,$$

i.e. with formation of hydrogen iodide. On the basis of kinetic data and on the assumption that reaction of trialkylsilanes with iodine does indeed proceed in accordance with the above equation, Deans and Eaborn [4, 5] concluded that the reaction is of the fourth (!) order.

As we doubted the correctness of these conclusions, we undertook an investigation of the reaction of trialkylsilanes with iodine. Our objects included also the preparation of some pure trialkyliodosilanes and the determination of their physical constants. We found that trialkylsilanes react readily and smoothly with iodine, both in a solvent medium (petroleum ether, carbon tetrachloride, etc.), and also in absence of solvent, with formation of the corresponding trialkyliodosilanes in 90-94% yield. The reaction was carried out by gradual addition of iodine to the trialkylsilane, as such or as a solution, at a molar ratio $I_2 : R_3SiH = 0.6$. Reaction was accompanied by the evolution of hydrogen (and not hydrogen iodide), and this was formed in almost theoretical amount.

This fact, and also the fact that only one-half of a molecular equivalent of iodine is necessary for the complete conversion of one molecular equivalent of trialkylsilane into trialkyiodosilane, indicates beyond doubt that reaction does not proceed in the way previously assumed, but in accordance with the overall equation:

$$2R_3SiH + I_2 \longrightarrow 2R_3SiI + H_2.$$

Evolution of hydrogen iodide (in addition to hydrogen) can be observed only when the order in which the reactants are added is reversed, i. e. when the trialkylsilane is added to excess of iodine, as was done by Eaborn in one of his investigations [3].

Our results show that, when trialkylsilanes are treated with iodine, two consecutive reactions occur:

$$R_3SiH + I_2 \longrightarrow R_3SiI + HI,$$

$$R_3SiH + HI \longrightarrow R_3SiI + H_2,$$

the hydrogen iodide liberated in the first reaction being capable of reacting almost completely with the trialkylsilane before leaving the sphere of reaction.

To obtain final confirmation of this scheme of reaction, we studied the reaction of trialkylsilanes with hydrogen iodide in absence of catalysts, and, as was expected, this led to the formation of the corresponding trialkyliodosilanes, the yields being 80-90%. In their investigations, Eaborn and Deans did not take account of the

* This reaction has been used also for the quantitative determination of trialkylsilanes [7].

Solvents: Petroleum ether, b. p. 60-80° was freed from unsaturated hydrocarbons by treatment with sulfuric acid and was then distilled over sodium. Carbon tetrachloride was distilled over phosphoric oxide.

TABLE 1

Trialkyliodosilanes R_3SiI

No.	R_3SiI	B. p. in °C (p in mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$	Iodine content (%) Found	Iodine content (%) Calculated	B.p. of unpurified substance in °C (p in mm)	Yield of unpurified substance (%)
1	$(C_2H_5)_3SiI$ * . . .	191.2(760)	1.351	1.4949	0.0127	52.66; 52.84	52.39	186—189 (756)	91
2	$(n\text{-}C_3H_7)_3SiI$ ** .	237.8(760)	1.229	1.4880	0.0120	44.71; 44.35	44.65	230—233.5 (751)	91
3	$(n\text{-}C_4H_9)_3SiI$ . .	119.3—119.7(2,5)	—	—	—	38.65; 39.20	38.89	277.5—280.5 (748)	91
4	$(i\text{-}C_5H_{11})_3SiI$ . .	140—140.5(2.5)	1.117	1.4842	0.0102	34.49; 34.93	34.45	139—142 (2,5)	94
5	$(n\text{-}C_6H_{13})_3SiI$ . .	185—186(3)	1.086	1.4810	0.0110	30.49; 30.52	30.92	183.5—189 (3)	90

* Data in literature [14]: b. p. 193°; d_4^{20} 1.333; [1]: b. p. 191.5° (752.4 mm); d_4^{20} 1.354; n_D^{20} 1.4925.

** Data in literature [12]: b. p. 235°; d~1.2; [1]: b. p. 235.3° (734.0 mm).

TABLE 2

Properties of Trialkylsilanes R_3SiH

R_3SiH	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$
$(C_2H_5)_3SiH$ *	108,2 (760)	0,7310	1,4120	0,0081
$(n\text{-}C_3H_7)_3SiH$ *	173,2 (760)	0,7598	1,4278	0,0082
$(n\text{-}C_4H_9)_3SiH$ *	89,0 (5)	0,7794	1,4380	0,0083
$(i\text{-}C_5H_{11})_3SiH$	94,4 (1)	0,7846	1,4407	0,0084
$(n\text{-}C_6H_{13})_3SiH$	160,5—161,0 (5)	0,7992	1,4480	0,0083

* Data in literature [15, 16].

Experimental Procedure

All experiments on the reaction of trialkylsilanes with iodine were carried out in a distilling flask fitted with a 20-cm Vigreux column and having a capacity of 100-150 ml. A solution of 0.1 mole of the trialkylsilane in 50 ml of petroleum ether or carbon tetrachloride was placed in the flask, and iodine powder (0.12-0.125 g-atom) was added in small portions from an ampoule. The distillation flask was connected to a Liebig condenser and receiver, which was further connected through a Tishchenko vessel containing concentrated sulfuric acid to a gas

possibility of reaction between trialkylsilanes and hydrogen iodide, although it had been shown as early as 1939 that iodine may replace hydrogen attached to silicon when SiH_4 reacts with HI in presence of AlI_3 [8, 9].

In view of the fact that replacement of silicon-attached hydrogen by halogen under the action of hydrogen halides is catalyzed by the corresponding aluminum halides [8-10], we studied the catalytic effect of aluminum iodide on the reactions of trialkylsilanes with iodine and hydrogen iodide. It was found that the reaction rate was considerably increased (by about 20-30%) in presence of small amounts of aluminum iodide, but the yields of trialkyliodosilanes were unchanged. It should be noted that, when the reaction of a trialkylsilane with iodine in presence of aluminum iodide is carried out in a carbon tetrachloride medium, a mixture of trialkyliodo- and trialkylchloro-silanes is formed owing to the occurrence of a catalytic exchange reaction with the solvent. It is therefore preferable to carry out syntheses of this sort in a petroleum ether medium.

The rate of reaction of a trialkylsilane with iodine or with hydrogen iodide diminishes as the length or ramification of the alkyl radical increases (iodination of tripropylsilane is five times as fast as that of triisopropylsilane [4, 5]). At the same time the polarization of the bond $\overset{\delta+}{Si}\text{—}\overset{\delta-}{H}$ must increase, i. e. the ease of its heterolytic fission, and therefore reactivity, must increase, so that the reaction of a trialkylsilane with iodine must be regarded as bimolecular nucleophilic replacement (S_N2 according to Ingold and Hughes), the mechanism of which can be represented as follows:

$$I^- + R_3SiH \rightarrow [I \ldots R_3Si \ldots H]^- \begin{cases} \xrightarrow{+I_2} R_3SiI + HI + I^- \\ \xrightarrow{+HI} R_3SiI + H_2 + I^- \end{cases}$$

This scheme indicates that reaction proceeds autocatalytically under the action of I^- ions.

Unlike this reaction, the reaction of trialkylsilanes with hydrogen bromide or chloride does not occur in absence of catalysts. We showed, for example, that in the reaction of triethylsilane with bromine no evolution of hydrogen could be detected, the process occurring strictly in accordance with the equation:

$$R_3SiH + Br_2 \rightarrow R_3SiBr + HBr,$$

The yield of bromotriethylsilane was 90%. This behavior can be explained by the fact that the affinities of bromine and chlorine for hydrogen are considerably greater than the affinity of iodine, so that the energy of the H—I bond (71.4 cal/mole) is less than that of the Si—H bond (75.0 cal/mole), whereas the energies of the H—Br and H—Cl bonds are greater (87.3 and 109.7 cal/mole, respectively) than that of the Si—H bond.

As there are no by-products, the reaction of trialkylsilanes with iodine makes it possible to prepare trialkyliodosilanes in a high degree of purity, which gives this method an advantage over other methods for their synthesis [11-13]. By treating trialkylsilanes with iodine we synthesized five pure trialkyliodosilanes, three of which were previously unknown. Their properties (refractometric constants for R_3SiI are given for the first time), analytical figures, and yields are given in Table 1.

EXPERIMENTAL

Reactants

The trialkylsilanes were prepared by reaction between trichlorosilane and the corresponding alkylmagnesium halides; they were purified by distillation through a column (under reduced pressure for the high-boiling compounds). Their yields, physical constants, and analytical figures are given in Table 2.

Hydrogen iodide was prepared by reaction of iodine and red phosphorus with dilute hydriodic acid. It was carefully freed from entrained iodine by passage through a tube containing red phosphorus moistened with hydriodic acid, and it was dried over phosphoric oxide. Iodine and aluminum powders were the commercial chemically pure products.

holder for the collection of hydrogen. Reaction was brought about by warming the mixture to 30-40°, and was complete when the evolution of hydrogen ceased. The course of the reaction could be readily followed from the volume of hydrogen evolved, the yield being usually theoretical. Solvent was driven off, and the residue of trialkyliodosilane was distilled. Reaction was sometimes carried out in absence of solvent, and the yields were almost the same. In absence of solvent, however, reaction was very vigorous and part of the iodine escaped in the form of hydrogen iodide.

The reactions of trialkylsilanes with hydrogen iodide were carried out in a 100-ml three-necked round-bottomed flask fitted with tube for the passage of gas, thermometer, and reflux condenser connected through a calcium chloride tube to a gas holder for the collection of hydrogen. The trialkylsilane (0.1 mole) was placed in the flask, and this was warmed while a stream of dry hydrogen iodide, free from iodine, was passed through. The course of the reaction was followed both by the volume of hydrogen evolved and by the temperature of the reaction mixture, which, in the case of triethylsilane, rose to a maximum when the theoretical amount of hydrogen had been evolved. The resulting trialkyliodosilane was isolated by distillation.

The trialkyliodosilanes obtained were immediately redistilled at ordinary or reduced pressure in diffuse light over copper powder in an atmosphere of pure dry nitrogen. They were quickly sealed in nitrogen-filled ampoules, which were then kept in the dark. The analyses and physical determinations on the trialkyliodosilanes were carried out as quickly as possible after their preparation, suitable precautions being taken against the introduction of traces of moisture.

The method of determining iodine in trialkyliodosilanes is described in our previous paper [2]. We shall now describe some typical experiments.

Reaction of Triethylsilane with Iodine. Iodine (15.9 g, i. e. 0.125 g-atom) was added in small portions to 11.6 g (0.1 mole) of triethylsilane dissolved in 50 ml of petroleum ether. The mixture was heated until the evolution of hydrogen ceased (two hours); 1.11 liters of hydrogen was formed. Solvent was distilled from the reaction mixture, and the residue was distilled over copper powder in a nitrogen atmosphere in diffuse light. The yield of triethyliodosilane, b. p. 186-189° (756 mm), was 22.0 g (91%). When the synthesis was carried out under quite analogous conditions, but in presence of 0.05 g of aluminum powder, evolution of hydrogen (1.14 liters) ceased after 90 minutes. The yield of triethyliodosilane, b. p. 185-188.5° (757 mm), was again 22.0 g.

Reaction of Tripropylsilane with Iodine in a Carbon Tetrachloride Medium in Presence of Aluminum. Aluminum powder (0.05 g) was added to a solution of 15.8 g (0.1 mole) of tripropylsilane in 50 ml of carbon tetrachloride, and then 15.3 g (0.125 g-atom) of iodine was added in small portions. The mixture was heated until hydrogen ceased to be evolved (two hours); the amount of hydrogen formed was 0.9 liter. Solvent was driven off, and fractional distillation of the residue gave 2.1 g of chlorotripropylsilane, b. p. 198-205° (770 mm) and 13.0 g of iodotripropylsilane, b. p. 229-240° (770 mm).

When this reaction was carried out in absence of aluminum, formation of chlorotripropylsilane was not observed and the yield of iodotripropylsilane, b. p. 230-233.5° (751 mm), was 24.7 g (87%). When carbon tetrachloride was replaced by petroleum ether, the yield of iodotripropylsilane, b. p. 229.5-234.5° (751 mm) was 91%.

Reaction of Tributylsilane with Iodine. Iodine (19.3 g, i. e. 0.125 g-atom) was added in small portions to a solution of 20.0 g (0.1 mole) of tributylsilane in 50 ml of petroleum ether. The mixture was heated until the evolution of hydrogen ceased (2.5 hours); the amount of hydrogen formed was 1.12 liters. Solvent was distilled from the mixture, and the residue was distilled. The yield of tributyliodosilane, b. p. 277.5-288.5° (748 mm) was 29.7 g (91%). In another experiment the reaction mixture was vacuum distilled; the yield of tributyliodosilane, b. p. 123-126° (4 mm) was then 84%.

Reaction of Trihexylsilane with Iodine in Absence of Solvent. Iodine (7.45 g, i. e. 0.06 g-atom) was added in small portions to 14.3 g (0.05 mole) of trihexylsilane. The mixture was heated until hydrogen ceased to be evolved (two hours); the amount of hydrogen formed was 0.52 liter. Vacuum distillation of the product over copper powder in a nitrogen atmosphere and in diffuse light gave 18.3 g (89%) of trihexyliodosilane, b. p. 190-192.5° (5 mm).

Reaction of Triethylsilane with Hydrogen Iodide. A stream of dry hydrogen iodide free from iodine was passed for four hours at the rate of 8-10 bubbles per minute through boiling triethylsilane (21.0 g, i. e. 0.18 mole). In the course of this time 3.9 liters of hydrogen came off and the boiling point of the reaction mixture rose from 108° to 188°. Distillation of the reaction product gave 34.0 g (78.2%) of triethyliodosilane, b. p. 188-193°. After

redistillation the triethyliodosilane had b. p. 191.8° (760 mm); d_4^{20} 1.3512; n_D^{20} 1.4948; $n_F^{20} - n_C^{20}$ 0.0127.

Found %: I 52.60, 52.31. $C_6H_{15}SiI$. Calculated %: I 52.39.

Reaction of Triisopentylsilane with Hydrogen Iodide. A stream of dry hydrogen iodide free from iodine was passed for 7.5 hours through 24.3 g (0.1 mole) of triisopentylsilane heated to 186°. The volume of hydrogen evolved was 2.2 liters. Vacuum distillation of the reaction mixture gave 33.5 g (91%) of iodotriisopentylsilane, b. p. 128-129° (1.5 mm). After redistillation the iodotriisopentylsilane had b. p. 126-126.5° (1 mm); d_4^{20} 1.1177; n_D^{20} 1.4842

Found %: I 34.63, 34.50. $C_{15}H_{33}SiI$. Calculated %: I 34.45.

Bromination of Triethylsilane. A solution of 16.0 g (0.1 mole) of bromine in 20 ml of carbon tetrachloride was added dropwise to a stirred, cooled (0°) solution of 11.6 g (0.1 mole) of triethylsilane in 50 ml of carbon tetrachloride. The added bromine was immediately decolorized until the theoretical amount had been added. There was vigorous evolution of hydrogen bromide, but no hydrogen was evolved.

After removal of solvent, distillation of the reaction mixture gave 17.5 g (90%) of bromotriethylsilane, b. p. 163-164° (736 mm). After redistillation through a column it had b. p. 166.3° (760 mm); d_4^{20} 1.1454; n_D^{20} 1.4573; $n_F^{20} - n_C^{20}$ 0.0088.

Found %: Br 41.11, 41.12. $C_6H_{15}SiBr$. Calculated %: Br 40.94.

SUMMARY

1. It was shown that reaction between trialkylsilanes and elementary iodine proceeds in accordance with the equation: $2R_3SiH + I_2 \rightarrow 2R_3SiI + H_2$.

2. Five trialkyliodosilanes, three of which were previously unknown, were synthesized in yields of 90-94%.

3. It was found that trialkyliodosilanes can be synthesized in high yield also by reaction between trialkylsilanes and hydrogen iodide, which occurs in absence of catalysts.

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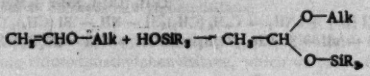
SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 4. SYNTHESIS OF THE METHYL, ETHYL, PROPYL, AND ISOPROPYL DIMETHYLPHENYLSILYL ACETALS OF ACETALDEHYDE

M. F. Shostakovsky and Kh. I. Kondratyev

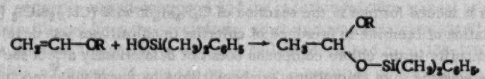
In previous papers Shostakovsky and coworkers [1-4] described the reaction between alkyl vinyl ethers and silanols, which results in the formation of mixed alkyl silyl acetals:



in which R is Alk or Ar.

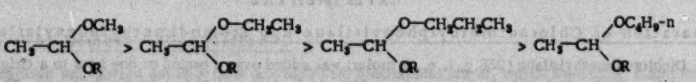
In the preceding investigation [4] we studied this reaction for an aliphatic-aromatic silanol and the vinyl ethers of butyl alcohol and its isomers with the object of finding the relation between structure and reactivity for these compounds. The present investigation forms a continuation of this work.

We studied the reaction between dimethylphenylsilanol and alkyl vinyl ethers:



in which R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7.

These investigations showed that the reactivity of the alkyl vinyl ether increases with increase in the size of the radical, when this is of normal structure, for the yields of the corresponding acetals increase in the series:

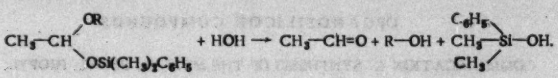


in which R is $-Si(CH_3)_2C_6H_5$.

When the alkyl radical is branched, the yield of acetal falls with increasing ramification:

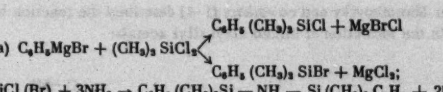
$$n\text{-}C_4H_9 > sec\text{-}C_4H_9 > t\text{-}C_4H_9;\quad n\text{-}C_3H_7 > i\text{-}C_3H_7.$$

The structure of the acetals was proved by hydrolysis:



We altered the hydrolysis conditions somewhat from those that we recommended previously [5].

Dimethylphenylsilanol was prepared [6, 7] by the following series of reactions:



We were the first to synthesize dimethylphenylsilanol in this way [4]. Its structure was confirmed both by the synthesis of the acetals enumerated above, and also by its conversion into symmetrical tetramethyldiphenyldisiloxane when distilled under normal pressure:

$$2C_6H_5(CH_3)_2SiOH \rightarrow C_6H_5(CH_3)_2SiOSi(CH_3)_2C_6H_5 + H_2O.$$

The symmetrical tetramethyldiphenyldisilazane that is formed in Stage (b) of the synthesis of the silanol was isolated in high yield and characterized for the first time. It was further confirmed that a mixture of chloro and bromo compounds is indeed formed in the reaction of C_6H_5MgBr with $(CH_3)_2SiCl_2$ [8], and a method for the quantitative determination of bromine in presence of chlorine in halosilanes was developed. The presence of bromo compound as impurity in the chloro compound does not deleteriously affect the course of the synthesis; nevertheless, we prepared some pure chlorodimethylphenylsilane by the method recommended by Dolgov and coworkers for the preparation of trialkylchlorosilanes [9]:

$$C_6H_5(CH_3)_2SiOSi(CH_3)_2C_6H_5 + AlCl_3 \rightarrow 2C_6H_5(CH_3)_2SiCl + AlOCl.$$

It follows that this method for the preparation of trialkylchlorosilanes from the corresponding hexaalkyldisiloxanes may be extended to the preparation of aliphatic-aromatic chlorosilanes.

EXPERIMENTAL

Preparation of Chlorodimethylphenylsilane and Bromodimethylphenylsilane

Dichlorodimethylsilane (258 g, i. e., 2 moles) was added over a period of one hour to a Grignard solution prepared from 52.8 g (2.1 moles) of magnesium, 680 ml of ether, and 314 g of bromobenzene. The liquid products were separated from the precipitate, ether was distilled off, and the residue was vacuum-fractionated. The chlorine and bromine contents of each fraction were determined by a method that is suitable when both halogens are present simultaneously: the overall content of chlorine and bromine was first determined by titration to phenolphthalein of a weighed portion (0.1-0.4 g) of the substance with 0.1 N NaOH (the sample was introduced into a flask containing 20 ml of water and 20 ml of ether); the aqueous layer was then separated, and its bromine

content was determined by the method described by Volyashko and others [10]. From the results of this analysis the contents of chlorodimethylphenylsilane and bromodimethylphenylsilane were calculated. The compositions of the fractions of the reaction product are given in Table 1.

TABLE 1

Fraction	B.p. in °C (p in mm)	Amount (g)	Content (%) of	
			$C_6H_5(CH_3)_2SiCl$	$C_6H_5(CH_3)_2SiBr$
I	71—74 (10)	27.1	81.2	Not determined
II	74—78 (10)	134.0	91.3	8.3
III	78—87 (10)	32.5	83.2	15.6
IV	87—98 (10)	25.6	63.2	33.0
V	98—132 (10)	9.0	15.3	51.7
VI	132—147 (10)	31.0	5.7	2.9

As will be seen from Table 1, Fractions II-IV consist almost entirely of a mixture of chloro- and bromodimethylphenylsilanes and can all equally well be used for the preparation of symmetrical tetramethyldiphenyldisilazane. Fraction II corresponds to chlorodimethylphenylsilane.

According to Lewis [8] chlorodimethylphenylsilane boils at 197° (766 mm) and the corresponding bromo compound at 215° (766 mm). Pure chlorodimethylphenylsilane, which we prepared by a method analogous to that of Dolgov and coworkers [9], had b. p. 195.5-197° (756.2 mm); d_4^{20} 1.0282; n_D^{20} 1.5002; found MR 48.90; calculated MR 49.58.

Found %: Cl 20.7
$C_8H_{11}ClSi$. Calculated %: Cl 20.8

Preparation of Symmetrical Tetramethyldiphenyldisilazane

Ether (260 ml) and Fraction II from the above-described experiment (75 g) were introduced into a three-necked flask fitted with mechanical stirrer, reflux condenser, thermometer, and tube for the passage of dry ammonia. The mixture was maintained at 0° and stirred while a stream of dry ammonia was passed. When reaction was complete, passage of ammonia was discontinued and the reaction mixture was set aside overnight. The liquid reaction products were filtered from the precipitate, ether and ammonia were distilled off, and the residue was vacuum distilled. A fraction amounting to 50 g was collected; it had b. p. 168-170° (9-10 mm) and 128-129° (2-3 mm); d_4^{20} 0.9850; n_D^{20} 1.5384; found MR 90.52; calculated MR 90.57; found M 283.8; calculated M 285.47.

Found %: C 67.92; 67.9; H 8.07; 7.94; N 4.94; 5.06; Si 19.54; 19.67.
$C_{16}H_{23}NSi_2$. Calculated %: C 67.31; H 8.12; N 4.92; Si 19.65.

On the basis of our results the substance isolated was symmetrical tetramethyldiphenyldisilazane (1,1,3,3-tetramethyl-1,3-diphenyldisilazane). It was obtained in 79.8% yield. It is hydrolyzed by water with formation of dimethylphenylsilanol or the condensation product of this compound, i. e., 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

Preparation of Dimethylphenylsilanol

The reaction was carried out in a flask provided with mechanical stirrer, reflux condenser, thermometer, and dropping funnel. A mixture of 100 ml of water, a few drops of methyl orange indicator, 250 ml of ether, and 74 g of 1,1,3,3-tetramethyl-1,3-diphenyldisilazane was prepared in the flask and was stirred vigorously while 0.5 N HCl was added dropwise until there was a stable pink coloration, the addition being at such a rate that a yellow color was maintained in the flask for 2.5-3 hours. The ether layer was separated and dried with potassium carbonate. Ether was distilled off, and vacuum distillation of the residue gave 62.6 g of a substance

having b. p. 99-99.5° (10 mm): d_4^{20} 0.9968; n_D^{20} 1.5120; found MR 45.81; calculated MR 45.86; found M 163; calculated M 152.36.

Found %: C 63.08; 62.94; H 7.73; 7.77; Si 18.49; 18.87.
$C_9H_{12}OSi$. Calculated %: C 63.11; H 7.95; Si 18.43.

The results indicate that the product was dimethylphenylsilanol, the yield being 79.25%. Dimethylphenylsilanol is a clear mobile liquid having a pleasant odor reminiscent of turpentine. On standing, it changes slowly with formation of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

Preparation of Symmetrical Tetramethyldiphenyldisiloxane

Dimethylphenylsilanol (30.4 g) was heated at normal pressure in a Wurtz flask with a bunsen flame. A distillate (26.1 g) of b. p. 277-280° (760 mm) or 106-107° (3 mm) was obtained; it had d_4^{20} 0.9086; n_D^{20} 1.5176; found MR 88.40; calculated MR 88.26; found M 284.4; calculated M 286.46.

Found %: C 67.45; 67.30; H 7.66; 7.84; Si 19.50; 19.23.
$C_{16}H_{22}OSi_2$. Calculated %: C 67.08; H 7.74; Si 19.59.

The results correspond to symmetrical tetramethyldiphenyldisiloxane (1,1,3,3-tetramethyl-1,3-diphenyldisiloxane), the yield being 91.28%. The literature [8] gives b. p. 110-111° (1 mm); d_4^{20} 0.9763; n_D^{20} 1.5122.

Preparation of Alkyl Dimethylphenylsilyl Acetals

a) Acetaldehyde Dimethylphenylsilyl Methyl Acetal $CH_3-CH(OCH_3)OSi(CH_3)_2C_6H_5$. At −8° to −10° a mixture was prepared of 7.7 g of dimethylphenylsilanol, 46.1 g of freshly distilled methyl vinyl ether (b. p. 5.5°; n_D^{20} 1.3730; d_4^{20} 0.7725), and one drop of 30% hydrochloric acid in an ampoule cooled in an ice-salt mixture. The ampoule was sealed and kept in a metal sleeve filled with water, which was maintained at 20° for 20 minutes and then at 30° for six hours. The ampoule was cooled and opened. The reaction products were neutralized with potassium carbonate and vacuum distilled from a Favorsky flask. The product was 7 g of a substance having b. p. 66-66.5° (1 mm); d_4^{20} 0.9694; n_D^{20} 1.4802; found MR 61.5; calculated MR 61.74; found M 209.16; calculated M 210.31.

Found %: C 63.17; 63.09; H 8.28; 8.49; Si 14.14; 14.06.
$C_{11}H_{18}OSi$. Calculated %: C 62.82; H 8.63; Si 13.34.

The results indicate that the product was acetaldehyde dimethylphenylsilyl methyl acetal, the yield being 65.9%. The dimethylphenylsilyl methyl acetal is a clear mobile liquid having a feeble ethereal odor; it is readily soluble in organic solvents.

b) Acetaldehyde Dimethylphenylsilyl Ethyl Acetal $CH_3-CH(OC_2H_5)OSi(CH_3)_2C_6H_5$. A mixture of 12 g ethyl vinyl ether (b. p. 36°; n_D^{20} 1.3779; d_4^{20} 0.7525) and 19 g of dimethylphenylsilanol was prepared in a 100-ml flask fitted with thermometer and reflux condenser and cooled with ice water. The mixture was cooled to a temperature of from −5° to −6°, and one drop of 30% hydrochloric acid was added. The cooling bath was removed and, when the temperature reached 34°, heating was applied for two hours, so that the temperature gradually rose to 42°. The reaction products were neutralized with potassium carbonate and subjected to fractional distillation. The fraction collected, amounting to 21.4 g, had b. p. 76-77° (2.5-3 mm); d_4^{20} 0.9542; n_D^{20} 1.4742; found MR 65.90; calculated MR 66.37; found M 220.6; calculated M 224.37.

Found %: C 64.35; 64.15; H 8.89; 8.95; Si 12.35; 12.13.
$C_{12}H_{20}OSi$. Calculated %: C 64.24; H 8.89; Si 12.51.

The results indicated that the product was acetaldehyde dimethylphenylsilyl ethyl acetal, obtained in 76.5% yield. The dimethylphenylsilyl ethyl acetal is a colorless mobile almost odorless liquid; it is readily soluble in organic solvents.

In a similar way we prepared the following acetals:

c) Acetaldehyde Dimethylphenylsilyl Propyl Acetal $CH_3CH(OCH_2CH_2CH_3)OSi(CH_3)_2C_6H_5$. For this we obtained b. p. 78-79° (2 mm); d_4^{20} 0.9439; n_D^{20} 1.4742; found MR 70.93; calculated MR 71.00; found M 231.8; calculated M 238.37; yield 86.5%.

Found %: C 65.41; 65.22; H 9.31; 9.15; Si 12.24; 12.30.
$C_{13}H_{22}O_2Si$. Calculated %: C 65.50; H 9.30; Si 11.77.

d) Acetaldehyde Dimethylphenylsilyl Isopropyl Acetal $CH_3CH(O{-}CH(CH_3)_2)OSi(CH_3)_2C_6H_5$. For this we obtained b. p. 74-76° (2 mm); d_4^{20} 0.9410; n_D^{20} 1.4737; found MR 71.10; calculated MR 71.00; found M 230.6; calculated M 238.37; yield 82.6%.

Found %: C 65.84; 65.70; H 9.49; 9.52; Si 11.74; 11.72.
$C_{13}H_{22}O_2Si$. Calculated %: C 65.50; H 9.30; Si 11.77.

Hydrolysis of Acetals

In order to hydrolyze the acetals, mixtures of 25 ml of 0.1 N sodium bisulfite, 10 ml of 2% sulfuric acid, and 0.2-0.4 g of the acetal were shaken in 100-ml ampoules for 6-8 hours at 18-20°. The excess of bisulfite was titrated with 0.1 N iodine. The results of the hydrolysis are shown in Table 2. The acetals investigated differed in the readiness with which they were hydrolyzed, the extent of hydrolysis diminishing in the following order: $CH_3 > i\text{-}C_3H_7 > C_2H_5 > n\text{-}C_3H_7$.

TABLE 2

Formula of acetal	Duration of shaking (hours)	Extent of of hydrolysis of acetal (%)
$CH_3CH(OCH_3)OSi(CH_3)_2C_6H_5$	6	93.01
$CH_3CH(OC_2H_5)OSi(CH_3)_2C_6H_5$	6	90.44
	8	93.58
$CH_3CH(OCH_2CH_2CH_3)OSi(CH_3)_2C_6H_5$	6	69.39
	6	71.76
	8	74.76
	8	75.18
$CH_3CH(O{-}CH(CH_3)_2)OSi(CH_3)_2C_6H_5$	6	91.14
	8	94.92

SUMMARY

1. The investigation established the effect of the structure and composition of the alkyl radical of an alkyl vinyl ether on the reactivity of the ether in the reaction of silyl acetal formation.

2. The following compounds were synthesized and characterized for the first time: a) methyl, ethyl, propyl, and isopropyl dimethylphenylsilyl acetals of acetaldehyde; b) 1,1,3,3-tetramethyl-1,3-diphenyldisilazane.

3. Chlorodimethylphenylsilane was prepared by a new method.

4. A new method was proposed for the determination of halogens in mixtures of chloro- and bromo-silanes.

5. The method of hydrolyzing acetals was improved.

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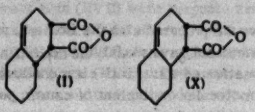
* T.p. = C. B. Translation pagination.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 11. STEREOCHEMISTRY OF 1,2,3,5,6,7,8,8a-OCTAHYDRO-1,2-NAPHTHALENEDICARBOXYLIC ACIDS

I. N. Nazarov, V. F. Kucherov and V. M. Andreev

In the preceding communication [1] we showed that in the condensation of maleic anhydride with 1-vinyl-1-cyclohexene two isomeric cis anhydrides (I) and (X) are formed, the difference between them lying in the disposition of hydrogen at C-8a.



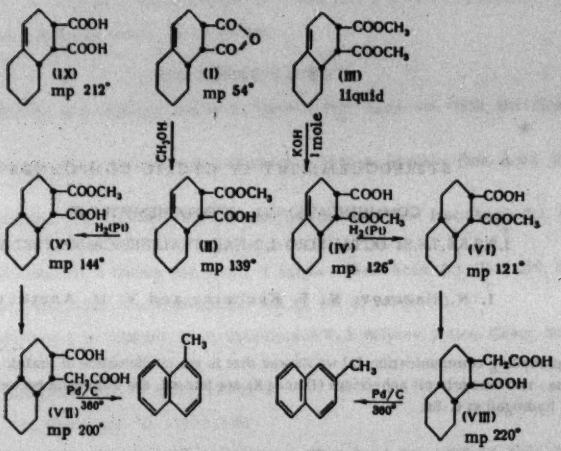
(I) (X)

In order to confirm their configurations, and also to investigate the stereochemistry of 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids, we studied the isomerization of cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids into the corresponding acids having a trans arrangement of the carboxyls. For this purpose it was most convenient to use the monoesters of these acids, which, when boiled with sodium methoxide in order to induce isomerization at the esterified carboxyl, should give the corresponding trans isomers having a definite spatial configuration of the carboxy groups. We prepared monoesters of the isomeric cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids by methods that we have developed [2]: reaction of anhydrides with methanol and partial hydrolysis of diesters [2]. It was found that for syn-cis- and anti-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids these reactions are sterically specific, and owing to the steric nonequivalence of the carboxyls they enable the two isomeric monoesters to be prepared.

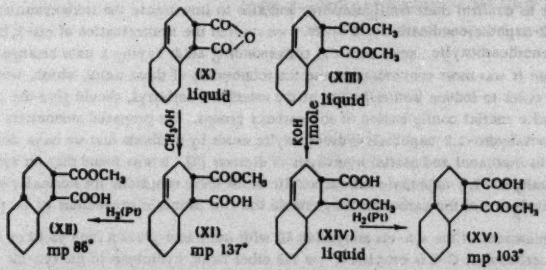
Thus, treatment of the syn-cis anhydride (I) with methanol gives a high yield of the syn-cis monoester (II), in which the carboxyl at C-2 is esterified; on the other hand, hydrolysis of the syn-cis diester (III) with one molecular equivalent of caustic potash gives mainly the isomeric syn-cis monoester (IV), in which the carboxyl at C-1 is esterified. The structures of these monoesters were proved by hydrogenation to the corresponding saturated cis-syn-cis monoesters (V) and (VI), which were converted by the Arndt-Eistert reaction into the isomeric carboxydecahydronaphthaleneacetic acids (VII) and (VIII), the dehydrogenation of which over palladized charcoal gave 1- and 2-methylnaphthalenes. As in the case of analogous compounds [1, 3], hydrogenation of the isomeric monoesters (II) and (IV) proceeds in a sterically selective fashion from the side opposite to the carboxyls with formation of the saturated monoesters (V) and (VI) of the cis-syn-cis series.

In this way, the monoester (II) was converted into cis-2-carboxydecahydro-1-naphthaleneacetic acid (VII), dehydrogenation of which gave 1-methylnaphthalene. Similarly, the isomeric monoester (IV) gave cis-1-carboxydecahydro-2-naphthaleneacetic acid (VIII), which gave 2-methylnaphthalene on dehydrogenation.

These results show, in complete agreement with molecular models, that in the acid (IX) the carboxyl at C-2 is the less effectively screened.

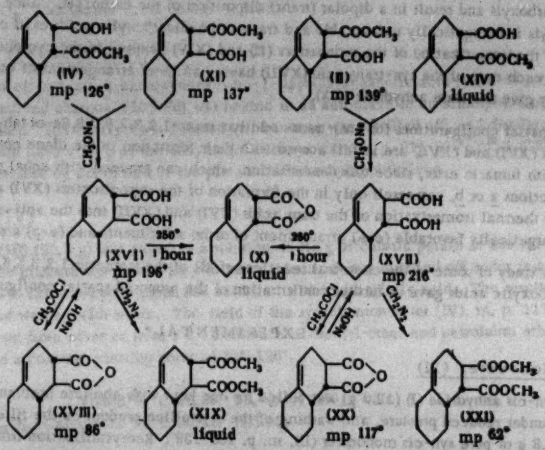


By the method described above we prepared also the isomeric monoesters of the anti-cis series. Treatment of the anti-cis anhydride (X) with methanol gave mainly the crystalline monoester (XI), which hydrogenated in a sterically selective fashion into the saturated trans-anti-cis monoester (XII), m. p. 86°. Selective hydrolysis of the anti-cis diester (XIII) with one molecular equivalent of caustic potash gave the liquid monoester (XIV), the hydrogenation of which gave the crystalline trans-anti-cis monoester (XV), m. p. 103°.



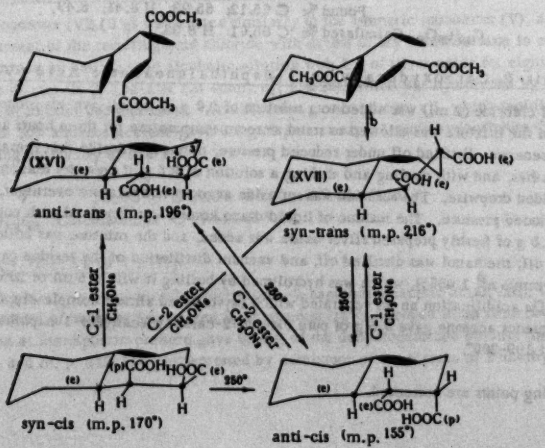
The isomeric monoesters (II), (IV), (XI), and (XIV) so obtained were subjected to trans isomerization with sodium methoxide at the boil, a process that is known to proceed only at esterified carboxyls and is a sterically specific method for the synthesis of trans-dicarboxylic acids. It was found that the monoesters (IV) and (XI) gave the same anti-trans acid (XVI), which formed the anhydride (XVIII) and the diester (XIX); on the other hand, the monoesters (II) and (XIV) gave the isomeric syn-trans acid (XVII), which formed the corresponding anhydride (XX) and diester (XXI).

It is not difficult to see that this can occur only when the corresponding monoesters (IV) and (XI), and also (II) and (XIV), are esterified on different carboxyls and are also epimeric with respect to hydrogen at C-8a. It follows that the original isomeric cis anhydrides (I) and (X) have the same respective configurations. The isomeric anti-trans- and syn-trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (XVI) and (XVII), and also their anhydrides (XVIII) and (XX) were found to have low thermal stability, each being isomerized in high yield to the same anti-cis anhydride (X) when heated for one hour at 250°.



The anti-trans acid (XVI) and syn-trans acid (XVII) were prepared also by direct diene synthesis from 1-vinyl-1-cyclohexene and dimethyl fumarate. The liquid adduct, which was formed in 88% yield, was found to be a mixture of isomeric trans diesters (XIX) and (XXI), from which hydrolysis and fractional crystallization gave small amounts of the pure trans acids (XVI) and (XVII). These acids are very close in solubility, and their separation is extremely difficult. However, from melting-point determinations on various mixtures of the pure isomers it was shown that in this diene synthesis the two possible trans isomers (XIX) and (XXI) are formed in the proportions of approximately 1 : 1 [4].

An examination of molecular models enabled us to obtain a clear picture of the character of the changes occuring and the spatial configurations of the isomeric trans acids (XVI) and (XVII). The models show that the isomerization of the syn-cis monoester (IV) at the esterified carboxyl at C-1 and of the anti-cis monoester (XI) at the esterified carboxyl at C-2 should occur very readily owing to the conversion of a polar (p) carboxyl group into an equatorial (e), the same anti-trans acid (XVI)—having a diequatorial (trans) arrangement of carboxyls – being formed in each case.



In the case of the isomeric monoesters (II) and (XIV), reaction with sodium methoxide should occur at the equatorial carboxyls and result in a dipolar (trans) disposition of the carboxyls. Since the (p-p) arrangement of the ortho carboxyls is energetically unfavorable and trans-ortho-dicarboxylic acids exist only in the (e-e) form [7], in the course of the isomerization of the monoesters (II) and (XIV) bending of the cyclohexene ring must occur with formation in each case of the syn-trans acid (XVII) having an (e-e) arrangement of carboxyls, by virtue of which it can readily give the trans anhydride (XX).

Such spatial configurations for anti-trans- and syn-trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (XVI) and (XVII) are in full accord with their formation in the diene condensation of 1-vinyl-1-cyclohexene with fumaric ester, since this condensation, which can proceed with equal probability in either of the possible directions a or b, can result only in the formation of the stereoisomers (XVI) and (XVII). This is in accord also with the thermal isomerization of the trans acids (XVI) and (XVII) into the anti-cis anhydride (X), which has the more energetically favorable (e-e) arrangement of ortho substituents and (e-p) arrangement of meta substituents.

Further study of some of the chemical reactions of all of the isomeric 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids gave us further confirmation of the proposed spatial configurations.

EXPERIMENTAL*

syn-cis Monoester (II)

The syn-cis anhydride (I) (12.0 g) was boiled for one hour with absolute methanol (60 ml). Methanol was distilled off under reduced pressure, and washing of the crystalline product on the filter with 60 ml of absolute ether gave 7.8 g of pure syn-cis monoester (II), m. p. 138-139°. Recrystallization from a large volume of ether did not affect the melting point. A further 0.7 g of the syn-cis monoester (II), m. p. 136-138°, could be isolated from the mother liquor by distilling off ether and recrystallizing the residue twice from ether.

Found %: C 65.78; 65.68; H 7.62; 7.52.
$C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53.

cis-syn-cis Monoester (V)

The syn-cis monoester (II) (7.8 g) was dissolved in absolute methanol (80 ml) and hydrogenated over 0.1 g of platinum oxide. One molecular equivalent of hydrogen (740 ml) was absorbed. The catalyst was filtered off, methanol was distilled off, and the crystalline residue was washed on the filter with ether. The product was 7.2 g of the cis-syn-cis monoester (V), m. p. 140-142°. When crystallized from a 6 : 1 mixture of ether and acetone it separated in large well-formed crystals having a constant melting point of 143-144°. No other crystalline product could be isolated from the ethereal mother liquor.

Found %: C 65.12; 65.23; H 8.41; 8.49.
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

cis-syn-cis-2-Carboxydecahydro-1-naphthaleneacetic Acid (VII)

Oxalyl chloride (2 ml) was added to a solution of 2.0 g of the cis-syn-cis monoester (V) in 20 ml of absolute benzene, and the mixture was allowed to stand at room temperature for three hours and then heated for 30 minutes at 50°. Benzene was distilled off under reduced pressure, the acid chloride that remained was dissolved in 10 ml of absolute ether, and with cooling and shaking a solution of 2.5 g of pure dry diazomethane in 150 ml of absolute ether was added dropwise. The solution was set aside at room temperature overnight, and ether was then distilled off under reduced pressure. The residue of liquid diazo ketone was dissolved with cooling in 40 ml of absolute methanol, 0.5 g of freshly prepared silver oxide was added, and the mixture was boiled for six hours. Silver oxide was filtered off, methanol was distilled off, and vacuum distillation of the residue gave 1.55 g of a diester (b. p. 141-143° (2 mm); n_D^{20} 1.4885), which was hydrolyzed by boiling it with 6.5 ml of 20% caustic potash solution for four hours. On acidification an oil separated which crystallized almost completely after a time. Crystallization from 50% aqueous acetone gave 0.5 g of pure cis-syn-2-carboxydecahydro-1-naphthaleneacetic acid (VII) melting constantly at 199-200°.

* All melting points are corrected.

Found %: C 64.96; 65.03; H 8.35; 8.41.
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

Dehydrogenation of the Acid (VII)

A mixture of 0.8 g of cis-syn-cis-2-carboxydecahydro-1-naphthaleneacetic acid (VII), 40 ml of cryoscopic benzene, and 0.5 g of palladized charcoal (10% Pd) was heated in an autoclave in an atmosphere of nitrogen (20 atm) at 360-370° for 20 hours. The catalyst was filtered off, benzene was distilled off, and distillation of the residue at atmospheric pressure gave 0.26 g of the dehydrogenation product, b. p. 210-215° (n_D^{20} 1.5760); its picrate had m. p. 139-140°, undepressed by admixture of the picrate of 1-methylnaphthalene.

syn-cis Monoester (IV)

The syn-cis diester (III) (25.3 g) was added to a solution of 5.5 g of caustic potash in 260 ml of methanol and 90 ml of water, and the mixture was boiled for two hours. Methanol was distilled off under reduced pressure, and the aqueous solution was extracted with ether and acidified with hydrochloric acid. The resulting crystalline product was filtered off and washed with water. The yield of the syn-cis monoester (IV), m. p. 117-121°, was 20.1 g. After crystallization from ether or from a 1 : 1 mixture of diethyl ether and petroleum ether, the syn-cis monoester (IV) had a constant melting point of 125-126°.

Found %: C 65.50; 65.45; H 7.60; 7.50.
$C_{13}H_{20}O_4$. Calculated %: C 65.52; H 7.53.

When the neutral ether extract was distilled, 2.2 g of the original syn-cis diester (III) was obtained.

cis-syn-cis Monoester (VI)

The syn-cis monoester (IV) (6.7 g) was dissolved in absolute methanol (70 ml) and hydrogenated in presence of 0.1 g of platinum oxide. One molecular equivalent of hydrogen (635 ml) was absorbed. The catalyst was filtered off, methanol was distilled off under reduced pressure, and the crystalline residue was washed on the filter with a little ether. The yield of cis-syn-cis monoester (VI), m. p. 121-123°, was 6.4 g. After crystallization from ether it was obtained as large clear crystals melting constantly at 120-121°; a mixture with the original monoester (IV) had a greatly depressed melting point (90-105°).

Found %: C 65.06; 65.04; H 8.35; 8.47.
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

cis-syn-cis-1-Carboxydecahydro-2-naphthaleneacetic Acid (VIII)

The cis-syn-cis monoester (VI) (2 g) was treated similarly to the isomeric monoester (V), and reaction with oxalyl chloride and treatment of the resulting acid chloride with excess of dry diazomethane in ether gave a diazo ketone, which was isomerized by boiling it in alcoholic solution with 1 g of silver oxide for eight hours. Distillation gave 1.36 g of the diester (b. p. 151-153° (at 4mm); n_D^{18} 1.4920), which was hydrolyzed by boiling it with 7 ml of 20% caustic potash solution for four hours. Acidification gave a viscous oil, which rapidly crystallized. Two crystallizations from 50% aqueous acetone gave 0.6 g of pure cis-syn-1-carboxydecahydro-2-naphthaleneacetic acid (VIII), melting constantly at 218-220°.

Found %: C 65.04; 65.03; H 8.28; 8.38.
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

Dehydrogenation of the Acid (VIII)

A mixture of 1.15 g of cis-syn-cis-1-carboxydecahydro-2-naphthaleneacetic acid (VIII), 0.5 g of palladized charcoal (10% Pd), and 20 ml of benzene was heated in an atmosphere of nitrogen in an autoclave at 360-370° for 20 hours. Distillation at atmospheric pressure gave 0.45 g of the dehydrogenation product (b. p. 215-225°; n_D^{20} 1.5790); its picrate had m. p. 112-113°, undepressed by admixture of the picrate of 2-methylnaphthalene.

anti-cis Monoester (XI)

A solution of 6.3 g of the anti-cis anhydride (X) in 60 ml of absolute methanol was boiled for one hour. Methanol was distilled off under reduced pressure, and the liquid residue was dissolved in a little petroleum ether. After two days the solution gave 3.8 g of crystals, m. p. 130-134°. Crystallization from a mixture of acetone and petroleum ether gave 3.5 g of pure anti-cis monoester (XI), melting constantly at 136-137°.

Found %: C 65.53; 65.62; H 7.61; 7.84.
$C_{13}H_{20}O_4$. Calculated %: C 65.52; H 7.53.

trans-anti-cis Monoester (XII)

The anti-cis monoester (XI) (4 g) was dissolved in absolute methanol (40 ml) and hydrogenated in presence of a platinum catalyst. After one molecular equivalent of hydrogen (380 ml) had been absorbed, the methanol was distilled off under reduced pressure. The liquid residue crystallized when treated with petroleum ether. The product was 3.5 g of trans-anti-cis monoester, m. p. 82-83.5°, which, after being crystallized from a mixture of petroleum ether with a little diethyl ether, melted constantly at 84-85°. No other hydrogenation products could be isolated.

Found %: C 64.75; 64.78; H 8.48; 8.50.
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

anti-cis Monoester (XIV)

The anti-cis diester (XIII) (4 g) was added to a solution of 0.8 g of caustic potash in 14 ml of water and 40 ml of methanol, and the mixture was boiled for two hours. Methanol was distilled off under reduced pressure, and the aqueous part was extracted with ether and acidified with hydrochloric acid. The liquid hydrolysis product, which did not crystallize on standing, was extracted with ether, and the extract was dried with sodium sulfate. Removal of ether by distillation gave 3 g of liquid anti-cis monoester (XIV), which we did not succeed in purifying, since it did not crystallize when cooled and treated with various solvents.

trans-anti-cis Monoester (XV)

The above-described liquid anti-cis monoester (XIV) (1.5 g) was dissolved in absolute methanol (20 ml) and hydrogenated over platinum oxide. One molecular equivalent of hydrogen (145 ml) was absorbed. The liquid hydrogenation product that remained after removal of methanol gradually crystallized when a mixture with petroleum ether was vacuum distilled. The crystalline product was filtered off and washed with petroleum ether. The yield of pure trans-anti-cis monoester (XV), m. p. 100-102°, was 0.95 g. After one crystallization from petroleum ether it melted constantly at 102-103°.

Found %: C 65.27; 65.20; H 8.55; 8.52.
$C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

anti-trans Dicarboxylic Acid (XVI)

a) The syn-cis monoester (IV) (0.8 g) was added to a solution of 1.9 g of sodium in 50 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in 35 ml of water. The solution was filtered and evaporated in a porcelain dish on a water bath to a thick slurry. The precipitate of salts was filtered off, washed with absolute methanol, and dissolved in 15 ml of water. The solution was acidified with hydrochloric acid, and the crystals that separated were filtered off. The product was 0.7 g of the anti-cis acid (XVI), m. p. 190-192°. After one crystallization from 25% aqueous acetone the acid melted constantly at 195-196°.

Found %: C 64.34; 64.25; H 7.14; 7.28.
$C_{12}H_{20}O_4$. Calculated %: C 64.27; H 7.19.

b) The anti-cis monoester (XI) (1 g) was added to a solution of 2.4 g of sodium in 8.5 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in 30 ml of water. The solution was filtered and evaporated down in a dish on a water bath. Treatment as before gave 0.65 g of pure anti-trans acid (XVI), m. p. 194-195°, identical with the sample obtained in the previous experiment.

syn-trans Dicarboxylic Acid (XVII)

a) The syn-cis monoester (II) (5.6 g) was added to a solution of 11.5 g of sodium in 330 ml of absolute methanol, and the mixture was boiled for 16 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in 275 ml of water. The solution was filtered and evaporated in a porcelain dish on a water bath. The salts were filtered off, washed with absolute methanol, and dissolved in 100 ml of water. The solution was filtered and acidified. The oil that separated rapidly solidified. The product was 4.5 g of the syn-trans acid (XVII), m. p. 210-212°, which melted constantly at 215-216° after crystallization from a little acetone.

Found %: C 64.33; 64.26; H 7.13; 7.30.
$C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

b) The liquid anti-cis monoester (XIV) (1.5 g) was added to a solution of 2.5 g of sodium in 90 ml of absolute methanol, and the solution was boiled for 15 hours. The crystalline product obtained by treatment as before was washed on the filter with 30% acetone and gave 0.75 g of the syn-trans acid (XVII), m. p. 210-212°, raised to 215-216° by crystallization from acetone; it was identical with the product of the previous experiment.

anti-trans Anhydride (XVIII)

A mixture of 0.9 g of the anti-trans acid (XVI) and 9 ml of acetyl chloride was boiled for 45 minutes. Acetyl chloride was distilled off, and the liquid residue was crystallized by repeatedly evaporating it down under reduced pressure with a mixture of benzene and petroleum ether. The crystals were washed on the filter with a 1 : 5 mixture of diethyl ether and petroleum ether. The product was 0.6 g of the anti-trans anhydride (XVIII), m. p. 80-82°, which melted constantly at 85-86° after crystallization from a 1 : 4 mixture of diethyl ether and petroleum ether.

Found %: C 69.88; 69.70; H 6.74; 6.96.
$C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84.

Hydrolysis of the anti-trans anhydride (XVIII) with 5% caustic soda solution gave a quantitative yield of the original anti-trans acid (XVI), m. p. 195-196°.

anti-trans Diester (XIX)

An ethereal solution of 1.5 g of the anti-trans acid (XVI) was treated with excess of diazomethane, and distillation gave 1.4 g of the anti-trans diester (XIX), b. p. 131-132° (2 mm); n_D^{20} 1.4936; d_4^{20} 1.1162; Found MR 65.73; Calculated MR 65.29.

Found %: C 66.60; 66.50; H 7.95; 8.00.
$C_{14}H_{20}O_4$. Calculated %: C 66.65; H 7.99.

syn-trans Anhydride (XX)

A mixture of 1.1 g of the syn-trans acid (XVII) and 10 g of acetyl chloride was boiled for one hour. The oily substance remaining after removal of acetyl chloride by distillation crystallized when repeatedly evaporated down under reduced pressure in admixture with benzene and petroleum ether. The product was 0.75 g of the syn-trans anhydride (XX), m. p. 114-117°, which melted constantly at 116-117° after crystallization from absolute ether.

Found %: C 70.09; 70.18; H 6.98; 7.07.
$C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84.

Hydrolysis of this anhydride with 5% caustic soda solution gave the original syn-trans acid (XVII), m. p. 215-216°.

syn-trans Diester (XXI)

A suspension of 0.5 g of the syn-trans acid (XVII) in ether was treated with excess of diazomethane, and removal of ether by distillation gave the crystalline syn-trans diester (XXI), m. p. 60-62°. After crystallization from a little petroleum ether, (XXI) melted constantly at 61-62°.

Found %: C 66.73; 66.76; H 7.96; 7.95.
$C_{14}H_{20}O_4$. Calculated %: C 66.65; H 7.99.

Condensation of 1-Vinyl-1-cyclohexene with Dimethyl Fumarate

A mixture of 10.4 g of dimethyl fumarate, 20 g of 1-vinyl-1-cyclohexene (2.5-fold excess), and 30 ml of benzene was heated in a sealed steel tube at 210-215° for 3.5 hours (in a nitrogen atmosphere and in presence of pyrogallol). Benzene was distilled off, and vacuum distillation of the residue gave 18 g of liquid adduct, b. p. 153-163° (6 mm). Redistillation with a column gave 16 g of a mixture of the trans diesters (XIX) and (XXI), b. p. 158-162° (7 mm) and n_D^{20} 1.4930. The yield was 88% on the amount of fumaric ester taken.

This mixture of trans diesters (10 g) was hydrolyzed for 8 hours at the boil with 30% caustic potash solution (50 ml). A small amount of undissolved material (dimer of vinylcyclohexene) was extracted with ether, and the aqueous solution was treated with charcoal and filtered. The solution was acidified, and an oil separated which gradually solidified; it was washed with water and vacuum dried. The product was 7.5 g of a mixture of the trans acids (XVI) and (XVII), m. p. 162-175°. This mixture was treated with 50 ml of ether, and the undissolved portion was filtered off (Fraction A, 2.8 g, m. p. 178-181°). The ethereal mother liquor was evaporated down to a volume of 15 ml and was then diluted with an equal amount of petroleum ether. Some crystals were precipitated (Fraction B, 2.7 g, m. p. 179-182°).

Fraction A was treated with 60 ml of boiling ether, and the undissolved part was filtered off; the product, amounting to 0.6 g, melted at 207-210°, and crystallization of this from acetone gave 0.4 g of pure syn-trans dicarboxylic acid (XVII), m. p. 214-215°, undepressed by admixture of the substance already obtained by the isomerization of the monoesters (II) and (XIV). Fraction B was recrystallized twice from a little of a 1 : 1 mixture of acetone and petroleum ether, and 0.5 g of crystals, m. p. 189-191°, was obtained. Recrystallization from a little acetone gave 0.4 g of pure anti-trans dicarboxylic acid (XVI), m. p. 193-194°, undepressed by admixture of the substance obtained by the isomerization of the monoesters (IV) and (XI).

Mixtures of the pure isomeric trans acids (XVI) and (XVII) in the proportions 1 : 1, 1 : 2, and 2 : 1 melted respectively at 163-173°, 177-180°, and 180-183°.

Thermal Isomerization of the trans Dicarboxylic Acids (XVI) and (XVII)

a) The anti-trans acid (XVI) (0.52 g) was heated in a current of nitrogen for one hour at 250° and then vacuum distilled. The product was 0.37 g of the anti-cis anhydride (X), b. p. 180-182° (9 mm) and n_D^{20} 1.5230. After hydrogenation over platinum, 0.25 g of the trans-anti-cis anhydride of m. p. 126-127° obtained previously [1] was obtained.

b) In a similar way, 0.44 g of the syn-trans acid (XVII) was heated for one hour at 250°, and distillation of the product gave 0.32 g of the liquid anti-cis anhydride (X), b. p. 189-191° (12 mm) and n_D^{20} 1.5235, the hydrogenation of which gave 0.2 g of the above-described trans-anti-cis anhydride, m. p. 127°.

SUMMARY

1. By the addition of methanol to the isomeric cis anhydrides (I) and (X) and by the partial hydrolysis of the cis diesters (III) and (XIII), all four of the isomeric monoesters (II), (IV), (XI), and (XIV) of syn-cis- and anti-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids were prepared.

2. It was shown that the isomerization of the monoesters (IV) and (XI) by means of sodium methoxide gives the anti-trans acid (XVI), whereas similar treatment of the monoesters (II) and (XIV) gives the isomeric syn-trans

acid (XVII). This proves the configurations of the isomeric cis anhydrides (I) and (X) as epimers with respect to the hydrogen at C-8a.

3. 1-Vinyl-1-cyclohexene was condensed with fumaric ester, and an 88% yield of a mixture of equal amounts of the anti-trans and syn-trans diesters (XIX) and (XXI) was obtained.

4. An examination of molecular models has enabled us to explain the spatial configurations of all four isomeric 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids and some of their reactions.

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* T.p. = C. B. Translation pagination.

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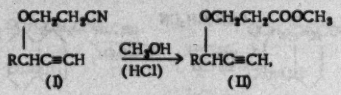
ACETYLENE DERIVATIVES

COMMUNICATION 175. ALCOHOLYSIS OF 2-CYANOETHYL ETHERS OF ACETYLENIC ALCOHOLS

I. N. Nazarov and G. A. Shvekhgeimer

There are no references in the literature to the alcoholysis of 2-cyanoethyl ethers of acetylenic alcohols. The method that we have developed for the alcoholysis of bis-2-cyanoethyl ethers of glycols [1] was found to be inapplicable for this case: concentrated sulfuric acid completely resinifies 2-cyanoethyl ethers of acetylenic alcohols. The alcoholysis of these ethers was successfully accomplished by boiling them with methanol saturated with dry hydrogen chloride. Their alcoholysis can be effected smoothly also by the action of a saturated solution of hydrogen chloride in methanol at room temperature.

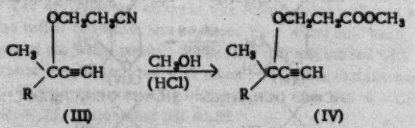
When 2-cyanoethyl ethers of secondary acetylenic alcohols (I) are boiled with methanol saturated with hydrogen chloride, the methyl esters (II) are obtained in 75-92% yield:



(I) (II)

R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7.

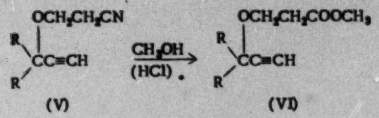
When 2-cyanoethyl ethers of tertiary acetylenic alcohols (III) are alcoholyzed under the same conditions, the yields of methyl esters (IV) fall progressively from 97% to 55% as the size of the radical in the alcohol increases. However, if this reaction is carried out under milder conditions – at room temperature for 24-60 hours – methyl esters (IV) carrying large radicals (R = n-C_6H_{13}, n-C_8H_{17}) may also be prepared in yields of more than 90%.



(III) (IV)

R = CH_3, C_2H_5, n-C_3H_7, n-C_6H_{13}, n-C_8H_{17}.

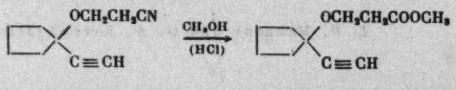
Increase in the size of both radicals in 2-cyanoethyl ethers of tertiary acetylenic alcohols (V) has a still greater deleterious effect on the alcoholysis, the yields of the methyl esters (VI) being only 45-32% when the reaction is carried out with heating and 75-65% when the reaction is carried out at room temperature.



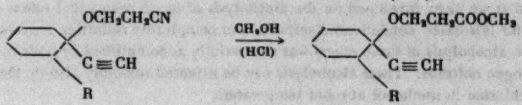
(V) (VI)

R = C_2H_5, n-C_3H_7.

The alcoholysis of the 2-cyanoethyl ethers of 1-ethynylcyclopentanol (VII) (proceeds at room temperature), 1-ethynylcyclohexanol (IX; R = H), and 2-ethynyldecahydro-2-naphthol (XI) proceeds smoothly with formation of the methyl ethers (VIII), (X; R = H), and (XII) in yields of more than 90%. Alcoholysis under the same conditions (with heating) of the 2-cyanoethyl ether of 1-ethynyl-2-methylcyclohexanol (IX; R = CH_3) gives the methyl ester (X; R = CH_3) in a yield of only about 60%.

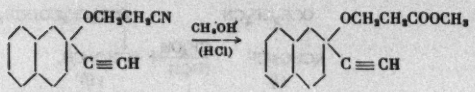


(VII) (VIII)



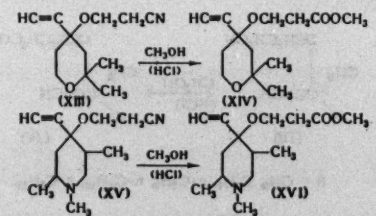
(IX) (X)

R = H, CH_3.



(XI) (XII)

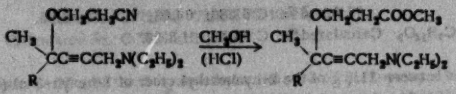
The 2-cyanoethyl ethers (XIII) and (XV) of heterocyclic acetylenic alcohols are readily converted by treatment with boiling methanolic hydrogen chloride into the methyl esters (XIV) and (XVI) in yields of 70-80%.



(XIII) (XIV)

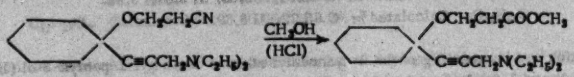
(XV) (XVI)

The alcoholysis of the 2-cyanoethyl ethers (XVII) and (XIX) also proceeds smoothly: the corresponding methyl esters (XVIII) and (XX) are formed in yields of more than 80-90%.



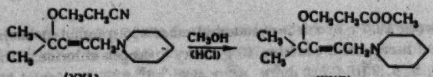
(XVII) (XVIII)

R = CH_3, C_2H_5.



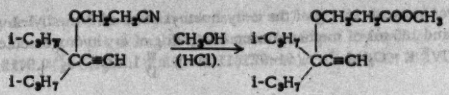
(XIX) (XX)

Instead of the diethylamine residue, the piperidine residue may be introduced:



(XXI) (XXII)

Alcoholysis of the 2-cyanoethyl ether of 3-isopropyl-4-methyl-1-pentyn-3-ol (XXIII) under mild conditions (without application of heat) results in the formation of the methyl ester (XXIV) in 58% yield:



(XXIII) (XXIV)

EXPERIMENTAL

Alcoholysis of 2-Cyanoethyl Ethers of Acetylenic Alcohols at the Boil

1) A mixture of 6 g of the 2-cyanoethyl ether of 3-butyn-2-ol (I; R = CH_3), b. p. 83-84° (12 mm), and 90 ml of methanol containing 20 g of dry hydrogen chloride was boiled under reflux in a round-bottomed flask for two hours in a water bath. The reflux condenser was replaced by a Wurtz still head, and methanol was removed at 50-60° under the vacuum of the water pump. Water (150 ml) was stirred with the residue, which was then saturated with potassium carbonate and extracted with ether. The ether extract was dried with magnesium sulfate and vacuum-fractionated. The product was 5.7 g of the methyl ester (II; R = CH_3), b. p. 85-86° (15 mm); n_D^{20} 1.4326; d_4^{20} 1.0005; found MR 40.19; calculated MR 40.38.

Found %: C 61.00; 61.04; H 7.69; 7.82.
$C_8H_{12}O_3$. Calculated %: C 61.54; H 7.69.

The alcoholysis of the 2-cyanoethyl ethers of the other acetylenic alcohols was carried out under similar conditions.

2) Reaction was between 10 g of the 2-cyanoethyl ether of 1-pentyn-3-ol (I; R = C_2H_5), b. p. 104-105° (15 mm), and 100 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 11 g of the methyl ester (II; R = C_2H_5), b. p. 95-96° (14 mm); n_D^{20} 1.4347; d_4^{20} 0.9822; found MR 45.14; calculated MR 44.99.

Found %: C 63.86; 64.08; H 8.22; 8.25.
$C_9H_{14}O_2$ Calculated %: C 63.53; H 8.23.

3) Reaction was between 11.5 g of the 2-cyanoethyl ether of 1-hexyn-3-ol (I; R = n-C_3H_7), b. p. 90-91° (6 mm), and 120 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 12.9 g of the methyl ester (II; R = n-C_3H_7), b. p. 104-105° (12 mm); n_D^{20} 1.4362; d_4^{20} 0.9678; found MR 49.72; calculated MR 49.61.

Found %: C 65.51; 65.58; H 8.67; 8.83.
$C_{10}H_{16}O_2$ Calculated %: C 65.22; H 8.69.

4) Reaction was between 8 g of the 2-cyanoethyl ether of 4-methyl-1-pentyn-3-ol (I; R = i-C_3H_7), b. p. 83-85° (5.5 mm), and 150 ml of methanol containing 18 g of dry hydrogen chloride. The product was 6.3 g of the methyl ester (II; R = i-C_3H_7), b. p. 95-96° (10 mm); n_D^{20} 1.4345; d_4^{20} 0.9646; found MR 49.70; calculated MR 49.61.

Found %: C 64.72; 64.86; H 8.68; 8.64.
$C_{10}H_{16}O_2$ Calculated %: C 65.22; H 8.69.

5) Reaction was between 13.7 g of the 2-cyanoethyl ether of 2-methyl-3-butyn-2-ol (III; R = CH_3), b. p. 100° (22 mm), and 130 ml of methanol containing 18 g of dry hydrogen chloride. The product was 16.6 g of the methyl ester (IV; R = CH_3), b. p. 83-84° (12 mm); n_D^{20} 1.4290; d_4^{20} 0.9698; found MR 45.19; calculated MR 44.99.

Found %: C 63.57; 63.69; H 8.36; 8.35.
$C_9H_{14}O_2$ Calculated %: C 63.53; H 8.23.

6) Reaction was between 15.1 g of the 2-cyanoethyl ether of 3-methyl-1-pentyn-3-ol (III; R = C_2H_5), b. p. 64° (2.5 mm), and 165 ml of methanol containing 25 g of dry hydrogen chloride. The product was 12.6 g of the methyl ester (IV; R = C_2H_5), b. p. 91-92° (11 mm); n_D^{20} 1.4338; d_4^{20} 0.9712; found MR 49.32; calculated MR 49.61.

Found %: C 65.62; 65.66; H 8.68; 8.79.
$C_{10}H_{16}O_2$ Calculated %: C 65.22; H 8.69.

7) Reaction was between 10 g of the 2-cyanoethyl ether of 3-methyl-1-hexyn-3-ol (III; R = n-C_3H_7), b. p. 112-114° (15 mm), and 120 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 6.9 g of the methyl ester (IV; R = n-C_3H_7), b. p. 104-105° (12 mm); n_D^{20} 1.4374; d_4^{20} 0.9594; found MR 54.11; calculated MR 54.23.

Found %: C 66.23; 66.71; H 9.41; 9.36.
$C_{11}H_{18}O_2$ Calculated %: C 66.66; H 9.09.

8) Reaction was between 10.5 g of the 2-cyanoethyl ether of 3-methyl-1-nonyn-3-ol (III; R = n-C_6H_{13}), b. p. 115-116° (2.5 mm), and 100 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 6.9 g of the methyl ester (IV; R = n-C_6H_{13}), b. p. 115-116° (3 mm); n_D^{20} 1.4423; d_4^{20} 0.9405; found MR 67.56; calculated MR 68.08.

Found %: C 70.24; 70.33; H 10.08; 10.16.
$C_{14}H_{24}O_2$ Calculated %: C 70.00; H 10.00.

9) Reaction was between 12 g of the 2-cyanoethyl ether of 3-methyl-1-undecyn-3-ol (III; R = n-C_8H_{17}), b. p. 148-150° (3.5 mm), and 100 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 8.7 g of the methyl ester (IV; R = n-C_8H_{17}), b. p. 146-148° (4 mm); n_D^{20} 1.4474; d_4^{20} 0.9164; found MR 78.19; calculated MR 77.32.

Found %: C 72.34; 72.17; H 10.83; 10.89.
$C_{10}H_{18}O_2$. Calculated %: C 71.64; H 10.45.

10) Reaction was between 10 g of the 2-cyanoethyl ether of 3-ethyl-1-pentyn-3-ol (V; R = C_2H_5), b. p. 111-113° (15 mm), and 120 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 5.4 g of the methyl ester (VI; R = C_2H_5), b. p. 105-107° (13 mm); n_D^{20} 1.4402; d_4^{20} 0.9671; found MR 54.00; calculated MR 54.23.

Found %: C 66.51; 66.63; H 9.14; 9.08.
$C_{11}H_{18}O_2$. Calculated %: C 66.66; H 9.09.

11) Reaction was between 10 g of the 2-cyanoethyl ether of 3-propyl-1-hexyn-3-ol (V; R = n-C_3H_7), b. p. 98-99° (4 mm), and 120 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was 3.8 g of the methyl ester (VI; R = n-C_3H_7), b. p. 125-127° (12 mm); n_D^{20} 1.4424; d_4^{20} 0.9537; found MR 62.75; calculated MR 63.47.

Found %: C 68.98; 68.83; H 9.72; 9.72.
$C_{13}H_{22}O_2$. Calculated %: C 69.02; H 9.73.

12) Reaction was between 17.5 g of the 2-cyanoethyl ether of 1-ethynylcyclohexanol (IX; R = H), b. p. 110-113° (3.5 mm), and 175 ml of methanol containing 27 g of dry hydrogen chloride. The product was 18.9 g of the methyl ester (X; R = H), b. p. 101-102° (2.5 mm); n_D^{20} 1.4652; d_4^{20} 1.0262; found MR 56.79; calculated MR 56.65.

Found %: C 68.81; 68.96; H 8.52; 8.60.
$C_{12}H_{18}O_2$. Calculated %: C 68.57; H 8.57.

13) Reaction was between 10 g of the 2-cyanoethyl ether of 1-ethynyl-2-methylcyclohexanol (IX; R = CH_3), b. p. 135-136° (10 mm), and 150 ml of methanol containing 18 g of dry hydrogen chloride. The product was 7.1 g of the methyl ester (X; R = CH_3), b. p. 107-108° (2.5 mm); n_D^{20} 1.4642; d_4^{20} 1.0079; found MR 61.35; calculated MR 61.41.

Found %: C 70.02; 69.89; H 8.92; 9.10.
$C_{13}H_{20}O_2$. Calculated %: C 69.64; H 8.93.

14) Reaction was between 12 g of the 2-cyanoethyl ether of 2-ethynyldecahydro-2-napthol (XI), b. p. 150-153° (4.5 mm), and 100 ml of methanol containing 18.5 g of dry hydrogen chloride. The product was the methyl ester (XII), b. p. 150-152° (4 mm); n_D^{20} 1.4887; d_4^{20} 1.0465; found MR 72.77; calculated MR 72.92.

Found %: C 73.36; 73.14; H 9.24; 9.28.
$C_{15}H_{24}O_2$. Calculated %: C 72.72; H 9.09.

15) Reaction was between 10.5 g of the 2-cyanoethyl ether of 4-ethynyltetrahydro-2,2-dimethylpyran-4-ol (XIII), b. p. 122-125° (3 mm), and 150 ml of methanol containing 18 g of dry hydrogen chloride. The product was 8.6 g of the methyl ester (XIV), b. p. 119-120° (2.5 mm); n_D^{20} 1.4647; d_4^{20} 1.0516; found MR 63.06; calculated MR 62.91.

Found %: C 65.21; 65.33; H 8.42; 8.51.
$C_{13}H_{20}O_4$. Calculated %: C 65.00; H 8.33.

16) Reaction was between 10 g of the 2-cyanoethyl ether of 4-ethynyl-1,2,5-trimethyl-4-piperidinol (XV), b. p. 135-137° (3 mm), and 90 ml of methanol containing 20 g of dry hydrogen chloride. The product was 9.1 g of the methyl ester (XVI), b. p. 123-125° (2 mm); n_D^{20} 1.4692; d_4^{20} 1.0252; found MR 68.75; calculated MR 69.82.

Found %: N 5.62; 5.81.
$C_{14}H_{23}NO_3$. Calculated %: N 5.53.

17) Reaction was between 13 g of the 2-cyanoethyl ether of 5-diethylamino-2-methyl-3-pentyn-2-ol (XVII; R = CH_3), b. p. 118-120° (3.5 mm), and 90 ml of methanol containing 25 g of dry hydrogen chloride. The product was 12.4 g of the methyl ester (XVIII; R = CH_3), b. p. 116-118° (2 mm); n_D^{20} 1.4504; d_4^{20} 0.9528; found MR 71.98; calculated MR 72.03.

Found %: N 5.78; 5.82.
$C_{14}H_{25}O_3N$. Calculated %: N 5.49.

18) Reaction was between 13 g of the 2-cyanoethyl ether of 1-(3-diethylamino-1-propynyl)cyclohexanol (XIX), b. p. 168-170° (6 mm), and 90 ml of methanol containing 20 g of dry hydrogen chloride. The product was 12.8 g of the methyl ester (XX), b. p. 155-157° (3 mm); n_D^{20} 1.4744; d_4^{20} 0.9894; found MR 83.85; calculated MR 83.68.

Found %: N 4.88; 5.03.
$C_{17}H_{29}NO_3$. Calculated %: N 4.74.

Alcoholysis of 2-Cyanoethyl Ethers of Acetylenic Alcohols at Room Temperature

1) A mixture of 8 g of the 2-cyanoethyl ether of 3-methyl-1-hexyn-3-ol (III; R = n-C_3H_7) and 100 ml of methanol containing 19 g of dry hydrogen chloride was left in a round-bottomed flask for 60 hours at room temperature. The flask was fitted with a Wurtz still head, and methanol was removed under the vacuum of the water pump at 25-30°. Water (150 ml) was added to the residue, and the mixture was stirred and saturated with potassium carbonate. The product was extracted with ether and dried with magnesium sulfate. Vacuum fractionation gave 8.2 g of the methyl ester (IV; R = n-C_3H_7), b. p. 80-82° (2.5 mm).

Alcoholysis at room temperature was carried out on 2-cyanoethyl ethers of the other acetylenic alcohols under similar conditions.

2) Reaction was between 8 g of the 2-cyanoethyl ether of 3-methyl-1-nonyn-3-ol (III; R = n-C_6H_{13}) and 100 ml of methanol containing 18 g of dry hydrogen chloride. The product was 8.4 g of the methyl ester (IV; R = n-C_6H_{13}), b. p. 118-120° (3.5 mm).

3) Reaction was between 8 g of the 2-cyanoethyl ether of 3-methyl-1-undecyn-3-ol (III; R = n-C_8H_{17}) and 100 ml of methanol containing 18 g of dry hydrogen chloride. The product was 8.5 g of the methyl ester (IV; R = n-C_8H_{17}), b. p. 145-147° (3.5 mm).

4) Reaction was between 8.5 g of the 2-cyanoethyl ether of 2-ethyl-1-pentyn-3-ol (V; R = C_2H_5) and 100 ml of methanol containing 19 g of dry hydrogen chloride. The product was 9 g of the methyl ester (VI; R = C_2H_5), b. p. 103-104° (10 mm).

5) Reaction was between 8 g of the 2-cyanoethyl ether of 3-propyl-1-hexyn-3-ol (V; R = n-C_3H_7) and 100 ml of methanol containing 19 g of dry hydrogen chloride. The product was 7.6 g of the methyl ester (VI; R = n-C_3H_7), b. p. 123-125° (11 mm).

6) Reaction was between 10 g of the 2-cyanoethyl ether of 1-ethynylcyclopentanol (VII), b. p. 125-127° (14 mm), and 100 ml of methanol containing 18 g of dry hydrogen chloride; duration of reaction 25 hours. The product was 10.8 g of the methyl ester (VIII), b. p. 98-100° (4 mm); n_D^{20} 1.4625; d_4^{20} 1.0302; found MR 52.35; calculated MR 52.03.

Found %: C 67.21; 67.39; H 8.11; 8.06.
$C_{11}H_{16}O_3$. Calculated %: C 67.35; H 8.16.

7) Reaction was between 8 g of the 2-cyanoethyl ether of 4-ethynyltetrahydro-2,2-dimethylpyran-4-ol (XIII) and 100 ml of methanol containing 18 g of dry hydrogen chloride; duration of reaction 24 hours. The product was 7.5 g of the methyl ester (XIV), b. p. 126-128° (3.5 mm).

8) Reaction was between 10 g of the 2-cyanoethyl ether of 2-methyl-5-piperidino-3-pentyn-2-ol (XXI), b. p. 146-147° (3 mm), and 110 ml of methanol containing 21 g of dry hydrogen chloride. The product was 10.6 g of the methyl ester (XXII), b. p. 145-146° (3 mm); n_D^{20} 1.4739; d_4^{20} 1.0056; found MR 74.60; calculated MR 74.44.

Found %: N 5.36; 5.47.
$C_{15}H_{25}NO_3$ Calculated %: N 5.24.

9) Reaction was between 20 g of the 2-cyanoethyl ether of 6-diethylamino-3-methyl-4-hexyn-3-ol (XVII; R = C_2H_5), b. p. 134-135° (3.5 mm), and 120 ml of methanol containing 25 g of dry hydrogen chloride. The product was 21.7 g of the methyl ester (XVIII; R = C_2H_5), b. p. 135-136° (4 mm); n_D^{20} 1.4520; d_4^{20} 0.9542; found MR 76.16; calculated MR 76.64.

Found %: N 5.14; 5.08.
$C_{15}H_{27}NO_3$ Calculated %: N 5.20.

10) Reaction was between 8 g of the 2-cyanoethyl ether of 3-isopropyl-4-methyl-1-pentyn-3-ol (XXIII), b. p. 126-128° (13 mm), and 100 ml of methanol containing 19 g of dry hydrogen chloride. The product was 6.8 g of the methyl ester (XXIV), b. p. 122-124° (14 mm); n_D^{20} 1.4446; d_4^{20} 0.9676.

Found %: C 68.78; 68.64; H 9.61; 9.64.
$C_{13}H_{22}O_3$ Calculated %: C 69.02; H 9.73;

SUMMARY

1. When treated with methanol and hydrogen chloride, 2-cyanoethyl ethers of secondary and tertiary acetylenic alcohols are readily converted into the corresponding methyl esters in high yield.

2. The yields of methyl esters are often increased considerably by carrying out the alcoholysis at room temperature.

LITERATURE CITED

[1] I. N. Nazarov, G. A. Shvekhgeimer, and V. A. Rudenko, J. Gen. Chem. 24, 329 (1954) (T.p. 269)*.

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* T.p. = C. B. Translation pagination.

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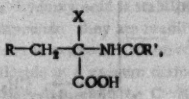
REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 11. α,β-DISUBSTITUTED α-ACYLAMINO CARBOXYLIC ACIDS

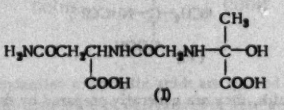
O. V. Kildisheva, M. G. Linkova, Z. V. Benevolenskaya, and I. L. Knunyants

The investigation of α-acylamino carboxylic acids having a group such as amino, hydroxy, or mercapto in the α-position, i. e.,



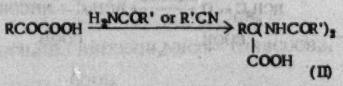
in which X = NH_2, NHCOR, NHR, OH, OR, SH, SR, presents considerable interest, for it is not improbable that such compounds enter into the composition of certain proteins, a view that receives indirect support from the fact that α-keto acids can be isolated from the hydrolyzates of some proteins.

It was shown fairly recently that 2-hydroxyalanine and 2-hydroxyvaline enter into the composition of the molecules of almost all ergot alkaloids [1, 2]; it is considered also [3] that a 2-hydroxyalanine residue is present in the molecule of the antibiotic lycomarasmine (I):



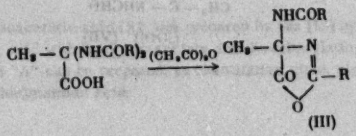
(I)

α,α-Bisacylamino carboxylic acids (II) have been known for a long time and are readily prepared by the condensation of keto acids with acid amides [4, 5] or nitriles [6]:



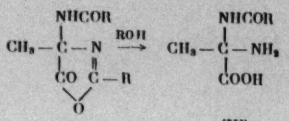
(II)

These acids are stable compounds; in aqueous solution they remain unchanged for several weeks, and they can be crystallized from alcohol without decomposition. By dehydration in presence of acetic anhydride they are readily converted into saturated oxazolinones (III) [6f, 7]:



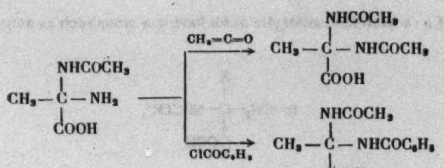
(III)

When these products are decomposed with alcohol in presence of moisture, α-acylamino α-amino carboxylic acids (IV) are formed [4, 6e]:



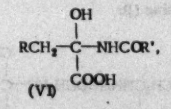
(IV)

Unlike 2,2-bisacylaminopropionic acids, α-acylamino α-amino carboxylic acids are unstable: they readily decompose in aqueous solution with formation of equivalent amounts of pyruvic acid and ammonia. However, 2-acetamido-2-aminopropionic acid reacts with ketene in aqueous N NaOH with formation 2,2-diacetamidopropionic acid, and it reacts with benzoyl chloride in sodium bicarbonate solution with formation of 2-acetamido-2-benzamidopropionic acid (V) [4]:



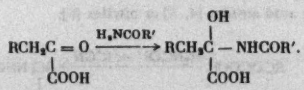
(V)

α-Acylamino α-hydroxy carboxylic acids (VI) are also known [8-13]:

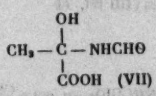


(VI)

Like α,α-bisacylamino carboxylic acids, they are generally prepared by the condensation of keto acids and amides, though under milder conditions:



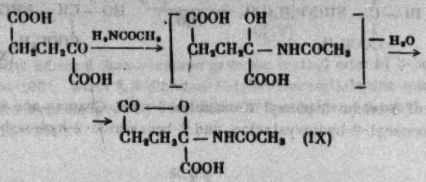
Equimolecular amounts of pyruvic acid and formamide will react at room temperature with formation of N-formyl-2-hydroxyalanine (VII) in quantitative yield [8]:



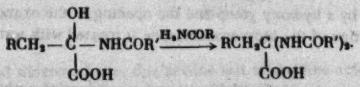
(VII)

Herbst [9] condensed pyruvic acid with acetamide and obtained N-acetyl-2-hydroxyalanine $CH_3C(OH)(COOH)NHCOCH_3$ (VIII) in the form of a molecular compound with two molecules of acetamide.

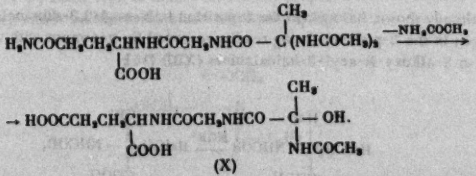
Condensation of 2-oxoglutaric acid with acetamide under mild conditions (not above 70°) gives the lactone of 2-acetamido-2-hydroxyglutaric acid (IX) [10]:



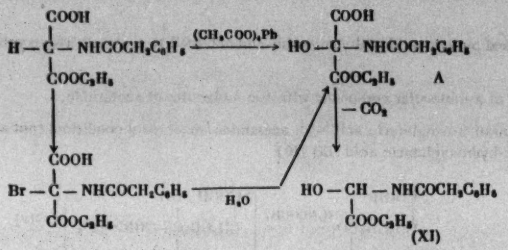
In this case the intermediate α-acylamino α-hydroxy acid is stabilized by lactone formation. α-Acylamino α-hydroxy carboxylic acids are unstable compounds; they are readily decomposed by water with formation of a keto acid and ammonia, and the hydroxy group is extremely reactive. Thus, for N-formyl-2-hydroxyalanine, it is only necessary to keep it over calcium chloride in a vacuum desiccator in order to remove the hydroxy group in the form of water and obtain 2-formamidoacrylic acid $CH_2=C(COOH)NHCHO$ [8]. In presence of excess of amide the hydroxy group is readily replaced by an amide residue with formation of α,α-bisacylamino carboxylic acids [10]:



When derivatives of α,α-bisacylamino carboxylic acids are treated with solutions of mineral acids, the acylamino groups are readily lost with formation of derivatives of keto acids [7]. Under milder hydrolysis conditions, only one amide residue may be removed; for example, hydrolysis of N^2-[N-(2,2-diacetamidopropionyl) glycyl]asparagine with 0.2 N HCl gave N-[N-(N-acetyl-2-hydroxyalanyl)glycyl]aspartic acid (X) [11]:

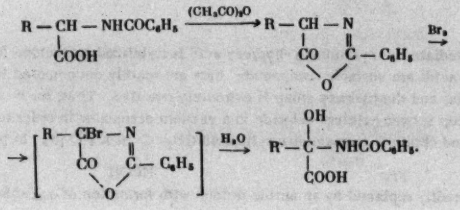


The ethyl ester of α-hydroxyphenaceturic acid (XI) was prepared by Sus [12] by oxidizing the monoethyl ester of (2-phenylacetamido)malonic acid with lead tetraacetate and decarboxylating the product, and Sus showed that the intermediate compound "A" can be prepared, in quantitative yield, also by hydrolysis of the monoethyl ester of bromo(2-phenylacetamido)malonic acid:



(XI)

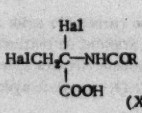
By the hydrolysis of 4-bromo-2-phenyl-2-oxazolin-5-ones, Chaman and Shelyakin [13] prepared N-benzoyl-2-hydroxyglycine, N-benzoyl-2-hydroxyalanine, and 2-benzamido-2-hydroxybutyric acid:



R = H, CH_3, C_2H_5.

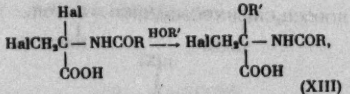
The replacement of bromine by a hydroxy group and the opening of the oxazolinone ring proceed simultaneously when the dichloroethane solution of the bromooxazolinone is treated with water; the bromooxazolinone is not isolated in the pure state.

The possibilities for the synthesis of multifunctional α-acylamino carboxylic acids are greatly extended now that the N-acyl-2,3-dihaloalanines (XII) recently synthesized by us [14] are available:



(XII)

As we have already shown, halogen in the 2-position in N-acyl-2,3-dihaloalanines is considerably more reactive than halogen in the 3-position, being readily removed by treatment with water or alcohols with formation of 2-hydroxy- or 2-alkoxy-N-acyl-3-haloalanines (XIII) [15]:

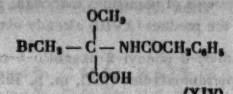


(XIII)

in which Hal = Cl, Br, R' = H, Alk; R = C_6H_5, $CH_2C_6H_5$.

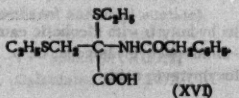
In the present investigation we continued our study of N-acyl-2,3-dihaloalanines and 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones.

Reaction of 2,3-dibromo-N-(phenylacetyl)alanine with methanol readily gave 3-bromo-2-methoxy-N-(phenylacetyl)alanine (XIV), m. p. 125-126°.



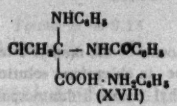
(XIV)

Treatment of the acid (XIV) with ethereal diazomethane gave the methyl ester of 3-bromo-2-methoxy-N-(phenylacetyl)alanine (XV), m. p. 104-106°. When 2,3-dibromo-N-(phenylacetyl)alanine was treated with excess of ethanethiol, both halogen atoms were replaced by ethylthio with formation of S-ethyl-2-(ethylthio)-N-(phenylacetyl)cysteine (XVI), m. p. 128-130°:



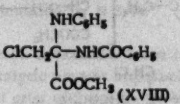
(XVI)

Treatment of N-benzoyl-2,3-dichloroalanine with aniline in ethereal solution readily gave the stable aniline salt of 2-anilino-N-benzoyl-3-chloroalanine (2-anilino-2-benzamido-3-chloropropionic acid) (XVII):



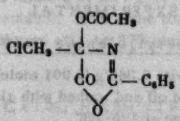
(XVII)

By treatment with ethereal diazomethane, this aniline salt or the free acid was converted into the methyl ester of 2-anilino-N-benzoyl-3-chloroalanine (XVIII), m. p. 126-128°:

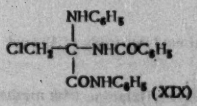


(XVIII)

Various derivatives of the same type of acid were readily prepared from 3-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one, which we had synthesized previously [14]:



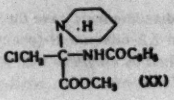
Investigation of the reactions of this oxazolinone with aniline showed that scission of the oxazolinone ring is accompanied by replacement of the acetoxy group. Thus, treatment of the oxazolinone with aniline in alcohol gave an 87% yield of the anilide of 2-anilino-N-benzoyl-3-chloroalanine (XIX), m. p. 139-140°:



(XIX)

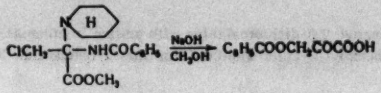
Reaction in presence of catalytic amounts of potassium carbonate gave the methyl ester of 2-anilino-N-benzoyl-3-chloroalanine, identical with the product (XVIII) already obtained.

Reaction of 3-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one with piperidine in alcohol gave the methyl ester of N-benzoyl-3-chloro-2-piperidinoalanine (XX), m. p. 103-104°:

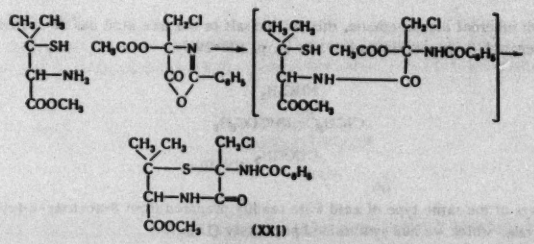


(XX)

The structure of (XX) was confirmed by its hydrolysis with alcoholic caustic soda to (benzoyloxy)pyruvic acid, which was isolated in the form of its 2,4-dinitrophenylhydrazone, m. p. 167°, identical with the 2,4-dinitrophenylhydrazone prepared from known (benzoyloxy)pyruvic acid.



Reaction between equimolecular amounts of the methyl ester of 3,3-dimethylcysteine and 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one in chloroform solution gave a cyclic peptide, the methyl ester of 6-benzamido-6-(chloromethyl)-2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic acid (XXI), m. p. 152-153°:



(XXI)

EXPERIMENTAL

3-Bromo-2-methoxy-N-(phenylacetyl)alanine (XIV)

Absolute methanol (2 ml) was mixed with 0.365 g (0.001 mole) of 2,3-dibromo-N-(phenylacetyl)alanine. The precipitate of the acid (XIV) was filtered off and washed with alcohol. After being precipitated from alcohol with water it melted with decomposition at 125-126°.

Found %: C 45.16; H 4.51; Br 25.82; N 4.10.
$C_{12}H_{14}O_4NBr$. Calculated %: C 45.60; H 4.42; Br 25.40; N 4.42.

Treatment of the acid (XIV) with ethereal diazomethane gave the methyl ester of 3-bromo-2-methoxy-N-(phenylacetyl)alanine (XV), m. p. 104-106°.

Found %: N 4.13.
$C_{13}H_{16}O_4NBr$. Calculated %: N 4.24.

S-Ethyl-2-(ethylthio)-N-(phenylacetyl)cysteine (XVI)

A mixture of 0.365 g (0.001 mole) of 2,3-dibromo-N-(phenylacetyl)alanine with excess of ethanethiol was left at room temperature until complete dissolution occurred (3-4 hours). Excess of ethanethiol was then removed in a vacuum. The residue crystallized when rubbed out with water. The product was 0.2 g of (XVI), m. p. 128-130° (from alcohol).

Found %: C 55.09; H 6.63; N 4.38.
$C_{15}H_{21}O_3NS_2$. Calculated %: C 55.04; H 6.42; N 4.28.

2-Anilino-N benzoyl 3-chloroalanine (XVII)

A solution of 1.68 ml (0.02 mole) of aniline in 5 ml of absolute ether was added gradually to a stirred solution of 2.62 g (0.01 mole) of N-benzoyl-2,3-dichloroalanine in 30 ml of absolute ether. The precipitate formed was filtered off and washed with water. The product was 2.1 g of the aniline salt of 2-anilino-N-benzoyl-3-chloroalanine (XVII), m. p. 120-121° (from methanol and ethyl acetate).

Found %: N 10.2.
$C_{22}H_{22}O_3N_3Cl$. Calculated %: N 10.2.

The aniline salt of (XVII) (0.2 g) was dissolved in saturated aqueous sodium bicarbonate. Aniline was removed by extraction with ether. The residue was acidified carefully in the cold with 2N HCl. The free acid (XVII), m. p. 90° (from ether), was obtained. It rapidly decomposed with keeping.

Found %: N 9.15.
$C_{16}H_{15}O_3N_2Cl$. Calculated %: N 8.79.

Methyl Ester of 2-Anilino-N-benzoyl-3-chloroalanine (XVIII)

a) The aniline salt (XVII) (0.41 g, i. e., 0.001 mole) was mixed with 5 ml of absolute ether and treated with excess of an ethereal solution of diazomethane. The product was the ester (XVIII), m. p. 125-126°.

Found %: N 8.46.
$C_{17}H_{17}O_3N_2Cl$. Calculated %: N 8.45.

b) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.26 g, i. e., 0.001 mole) was mixed with 2.5 ml of absolute methanol containing a catalytic amount of potassium carbonate, and 0.1 ml of aniline was added. The product was 0.15 g of the methyl ester of 2-anilino-N-benzoyl-3-chloroalanine, m. p. 126-128° (from ether). In admixture with the product of method (a) there was no depression of melting point.

Anilide of 2-Anilino-N-benzoyl-3-chloroalanine (XIX)

Aniline (2 ml) was added to a stirred mixture of 2.67 g (0.01 mole) of 4-acetoxy-4-(chloromethyl)-2-phenyl 2-oxazolin-5-one in 25 ml of absolute methanol. After some time complete dissolution occurred. A crystalline precipitate of (XIX) formed and was filtered off. An 87% yield of the acid (XIX), m. p. 139-140° (from alcohol), was obtained.

Found %: C 67.01; H 5.35; Cl 9.15; N 10.42.
$C_{22}H_{20}O_3N_3Cl$. Calculated %: C 67.09; H 5.08; Cl 9.02; N 10.67.

The mother liquor gave 0.3 g of (XVIII), m. p. 125-126°, undepressed by admixture of the substance obtained by method (a) (above).

Methyl Ester of N-Benzoyl-3-chloro-2-piperidinoalanine (XX)

A mixture of 0.53 g (0.002 mole) of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one and 2 ml of absolute methanol was treated with a solution of 0.004 mole of piperidine in 2 ml of methanol. Heat was evolved, and complete dissolution occurred. Alcohol was removed under reduced pressure, and (XX) was extracted with 25% sulfuric acid. The acid solution was neutralized with solid sodium bicarbonate, and the ester (XX), m. p. 103-104° (from ether), was obtained.

Found %: C 59.22; H 6.7; Cl 10.72; N 8.37.
$C_{16}H_{21}O_3N_2Cl$. Calculated %: C 59.10; H 6.47; Cl 10.94; N 8.62.

Methanolic caustic soda (1 ml of 2 N) was added to a mixture of 0.052 g of (XX) and 1 ml of absolute methanol. The mixture was left at room temperature until the next day, and alcohol was then removed under reduced pressure. The residue was dissolved in 2 ml of water and acidified with 2 N HCl. 2,4-Dinitrophenylhydrazine was added, and 0.06 g of the hydrazone of (benzoyloxy)pyruvic acid, m. p. 167°, was obtained. A mixture with an authentic sample showed no depression of melting point.

Methyl Ester of 6-Benzamido-6-(chloromethyl)-2,2-dimethyl-5-oxo-3-thiamorpholinecarboxylic Acid (XXI)

The methyl ester of 3,3-dimethylcysteine (7.2 g, i. e., 0.04 mole) was added to a solution of 11.8 g (0.04 mole) of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one in 60 ml of dry chloroform, and the mixture was heated at 40-45° for three hours. The solution was cooled, washed with N HCl and with water to remove unchanged dimethylcysteine ester, and dried over magnesium sulfate. Chloroform was removed under reduced pressure, and the residue was diluted with absolute ether. The crystalline precipitate then formed was filtered off and washed with ether. The product was 7.1 g of the peptide (XXI), m. p. 149°. A further 0.8 g of (XXI) was isolated from the mother liquor, the total yield being 48%. After being recrystallized from benzene the product melted with decomposition at 152-153°. The substance is readily soluble in alcohol, less readily soluble in benzene, and insoluble in ether and in water.

Found %: C 52.08; H 5.16; N 7.55.
$C_{15}H_{19}O_4N_2SCl$. Calculated %: C 51.82; H 5.12; N 7.56.

SUMMARY

1. It was shown that α-halo in α,β-dihalo α-acylamino carboxylic acids is replaced in reactions with amines and thiols with formation of α-acylamino carboxylic acids having a new substituent in the α-position.

2. It was shown that N-acyl-2,3-dihaloalanines can be converted into derivatives of 2-alkoxy- and 2-(alkylthio)-cysteine.

3. Various derivatives of the same acids were prepared by the action of amines and alcohols on 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one.

4. By the acylation of the methyl ester of 3,3-dimethylcysteine with 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one a peptide was obtained which was shown to be a derivative of α-substituted α-acylamino carboxylic acids.

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* T.p. = C. B. Translation pagination.

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ADDITION REACTIONS OF PERFLUOROOLEFINS

COMMUNICATION 5. CONJUGATED ADDITION OF HALOGENS

I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva

Addition of halogens to perfluoroolefins generally proceeds under the conditions of free-radical reactions. It is probably for this reason that conjugated-addition reactions between these substances, which would undoubtedly be ionic reactions, have not yet been brought about. However, it appears likely that reactions of this sort could occur under conditions such that the halogen molecule is strongly ionized, with increase in the nucleophilic character of the halogen anion. It was in fact found that many polyfluoroolefins readily combine with bromine in glacial acetic acid solution. When polyfluoroolefins were passed into a solution of bromine and mercuric acetate or sulfate in glacial acetic acid, acetoxybromopolyfluoroparaffins were formed. In particular, trifluoroethylene, 1,1-difluoroethylene, and others form esters of α,α-difluoro alcohols of formula $RCOCF_2R'$. Only one representative of this type of compounds has been described in the literature, namely, perfluorobutyrolactone $\begin{matrix}CF_2\text{—}CF_2\text{—}CF_2\\ O\text{———}CO\end{matrix}$ [1], which is an extremely reactive compound, reacting with water, ammonia, ethanol, and ethanethiol at about 0° with formation of compounds of the type

$$X\text{—}\overset{\overset{O}{\|}}{C}\text{—}CF_2\text{—}CF_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}X \quad (X = OH,\ OC_2H_5,\ NH_2,\ SC_2H_5).$$

Our preliminary investigations showed that 3,3,3-trifluoropropene, trifluoroethylene, and 1,1-difluoroethylene readily combine with bromine in glacial acetic acid solution with formation of the corresponding dibromides; in the case of 1,1-difluoro- and trifluoro-ethylenes, some acetoxy-bromo addition products are also formed. The readiness with which addition of bromine to fluoroolefins occurs in glacial acetic acid may be explained by increased polarization of the bromine molecule in the polar solvent with formation of Br_3^- and $Br_2CH_3COO^-$ complexes, which carry out an anionoid attack on the enfeebled π-bonds of the fluoroolefins.

When fluoroolefins were treated in glacial acetic acid solution with bromine in presence of mercuric acetate or sulfate, the reaction gave only acetoxy-bromo addition products, evidently owing to the preferential formation of the complex $Br_2CH_3COO^-$:

$$Br_2CH_3COO^- \ldots > \underset{CFH}{\overset{CF_2}{\|}} \longrightarrow \overset{\ominus}{\underset{CFH}{|}}\overset{CF_2OCOCH_3}{|}$$

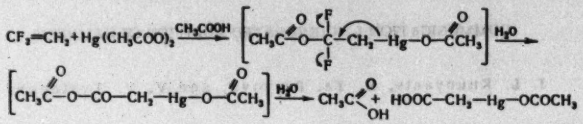
$$\overset{\ominus}{\underset{CFH}{|}}\overset{CF_2OCOCH_3}{|} + Br^+ \ldots Br^- \rightarrow \underset{CFHBr}{|}\overset{CF_2OCOCH_3}{|} + Br^-$$

$$Hg^{++} + 2Br^- \rightarrow HgBr_2.$$

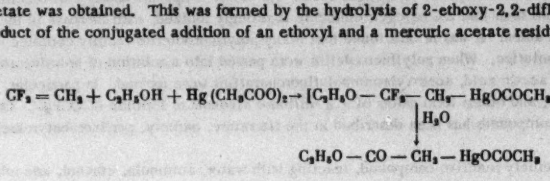
The formation of only acetoxy compounds under these conditions to the complete exclusion of dibromides caused us to doubt the correctness of the above mechanism. It naturally occurred to us that the first stage of the reaction might be the formation of an organomercury derivative of the fluoroolefin, which would be subsequently decomposed by bromine with formation of the acetoxy bromo compound. For verification purposes we investigated the behavior of the same olefins toward solutions of mercuric acetate in acetic acid, alcohol, and water.

Under these conditions we were unable to effect the addition of mercuric acetate to 3,3,3-trifluoropropene and to trifluoroethylene. Positive results were obtained only in the reaction of mercuric acetate with 1,1-difluoroethylene. The addition products then obtained were found to be extremely unstable compounds, readily converted into derivatives of (acetoxymercuri)acetic acid.

When 1,1-difluoroethylene was passed into a solution of mercuric acetate in glacial acetic acid, the gas was absorbed very rapidly and hydrogen fluoride soon began to be evolved; the other reaction product was (acetoxymercuri)acetic acid, the formation of which indicates the extreme readiness with which fluorine atoms in the β-position with respect to mercury are hydrolyzed.



When 1,1-difluoroethylene was passed into a solution of mercuric acetate in absolute ethanol, ethyl (acetoxymercuri)acetate was obtained. This was formed by the hydrolysis of 2-ethoxy-2,2-difluoroethylmercury acetate, the product of the conjugated addition of an ethoxyl and a mercuric acetate residue to 1,1-difluoroethylene:

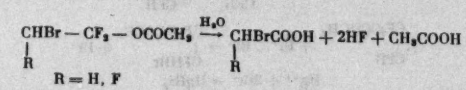


The negative results obtained for the addition of mercuric acetate to 3,3,3-trifluoropropene and trifluoroethylene refute the suggestion that mercury derivatives are formed as intermediaries and support the above-described mechanism of conjugated addition of bromine to fluoroolefins.

All of the acetoxy-bromo compounds obtained are readily soluble in organic solvents and are insoluble in water. Physical and analytical data for these compounds are given in the table. 2-Bromo-3,3,3-trifluoropropyl acetate is a stable colorless liquid having a pleasant ester odor. 2-Bromo-1,1-difluoroethyl acetate and 2-bromo-1,1,2-trifluoroethyl acetate are unstable colorless liquids having a sharp odor characteristic of anhydrides and producing irritation of the mucous membrane. When kept in a glass vessel they slowly decompose, but they can be kept for several months in a paraffined vessel without change.

Although there could be no doubt about the structures of the acetoxy-bromo compounds obtained, since they were determined by the well defined polarities of the reactants, it was nevertheless necessary to confirm these structures by experiment.

The structures of 2-bromo-1,1-difluoroethyl acetate and 2-bromo-1,1,2-trifluoroethyl acetate were proved by hydrolysis, the respective hydrolysis products being bromoacetic and bromofluoroacetic acids:



The formation of four molecular equivalents of acid in both cases was confirmed by titration with alkali (3.9 equivalents of caustic potash was required).

When 2-bromo-1,1,2-trifluoroethyl acetate was boiled with aqueous alkali, glyoxylic acid, isolated as the 2,4-dinitrophenylhydrazone, was obtained in 80% yield. This acid is formed as a result of the further hydrolysis

TABLE

No.	Fluoroolefin	Acetoxy-bromo addition product of fluoroolefin	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Analysis									
							Found					Calculated				
							MR	C (%)	H (%)	Br (%)	F (%)	*MR*	C (%)	H (%)	Br (%)	F (%)
1	$CF_2CH=CH_2$	$CF_2\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_2OCOCH_3$	78	149	1.3980	1.6352	34.70	25.05	2.57	34.50	23.4	34.68	25.53	2.55	34.04	24.25
2	$CF_2=CFH$	$CF_2\underset{\displaystyle OCOCH_3}{\underset{\vert}{C}}FHBr$	56	46 (30)	1.3820	1.70	30.25	21.98	1.82	36.05	25.11	30.21	21.72	1.81	36.20	25.79
3	$CF_2=CH_2$	$CF_2\underset{\displaystyle OCOCH_3}{\underset{\vert}{C}}H_2Br$	50	41 (20)	1.4030	1.6752	30.13	23.93	2.68	38.96	—	30.09	23.64	2.46	39.40	18.71

of bromofluoroacetic acid:

$$CFBrH{-}CF_2{-}OCOCH_3 \xrightarrow{H_2O} [CHFBrCOOH] \xrightarrow{H_2O} [HOCHFCOOH] \xrightarrow{-HF} HOC{\cdot}COOH$$

Analogous reactions of bromofluoroacetates are known [2].

In the cold, 2-bromo-1,1-difluoroethyl acetate does not react with absolute ethanol, but heating of the reaction mixture results in alcoholysis with formation of ethyl acetate, ethyl bromoacetate, and hydrogen fluoride:

$$CH_2Br-CF_2-OCOCH_3 \xrightarrow{C_2H_5OH} [CH_2Br-CF_2OH] + CH_3COOC_2H_5$$
$$[CH_2Br-CF_2OH] \xrightarrow{-HF} [CH_2Br-COF]$$
$$[CH_2Br-COF] \xrightarrow{C_2H_5OH} CH_2BrCOOC_2H_5$$

Hence, the acetoxy-bromo compounds that we obtained have the character of mixed anhydrides.

Apart from conjugated addition of bromine in acetic acid, we effected also the addition of bromine to 3,3,3-trifluoropropene and to trifluoroethylene in a medium of water. In presence of mercuric acetate, trifluoroethylene gave bromofluoroacetic acid:

$$CF_2=CHF + Br_2 + H_2O \xrightarrow{Hg(OAc)_2} [CFBrH-CF_2OH] \xrightarrow{-HF} [CFBrHCOF] \rightarrow$$
$$\rightarrow CFBrHCOOH$$

This is simpler as a method of preparation than that given in the literature [2] and may be a general method for the preparation of α-fluoro α-halo carboxylic acids. Under these conditions 3,3,3-trifluoropropene gave the bromohydrin, 2-bromo-3,3,3-trifluoro-1-propanol, b. p. 127°*:

$$CF_3CH=CH_2 + Br_2 + H_2O \xrightarrow{Hg(OAc)_2} CF_3CHBrCH_2OH.$$

The 1-naphthylurethan of this bromohydrin melted at 88°.

The development of convenient methods for the synthesis of 2-bromo-3,3,3-trifluoro-1-propanol and 2-bromo-3,3,3-trifluoropropyl acetate provided us with a simple synthesis for 2,3-epoxy-1,1,1-trifluoropropane, which has been previously obtained from trifluoroacetone [4]:

$$CF_3CHBrCH_2OCOCH_3 \xrightarrow{NaOH} CF_3-CH-CH_2$$
$$CF_3CHBrCH_2OH \xrightarrow{NaOH} \quad\quad O$$

EXPERIMENTAL

Addition of Bromine to 3,3,3-Trifluoropropene in Acetic Acid

A solution of 8 g of bromine in 25 ml of glacial acetic acid was stirred vigorously at room temperature, and 3,3,3-trifluoropropene was passed in until the solution was decolorized (1.25 liters). Reaction proceeded with evolution of heat. The reaction solution was diluted with an equal amount of water. The organic layer was separated and washed with water, with sodium carbonate solution, and again with water. The product was dried with calcium chloride. The yield of crude 2,3-dibromo-1,1,1-trifluoropropane was 10.3 g (82%). It had b. p.

* A patent published in 1955 described the formation of 2-bromo-3,3,3-trifluoro-1-propanol by the addition of hypobromous acid to 3,3,3-trifluoropropene [3].

114° and n_D^{25} 1.4300; the literature gives b. p. 115° and n_D^{25} 1.4286.

Addition of Bromine to 1,1-Difluoroethylene in Acetic Acid

Reaction of 0.75 liter of 1,1-difluoroethylene with bromine in accordance with the above procedure gave 3 g (43%) of 1,2-dibromo-1,1-difluoroethane, b. p. 94° and n_D^{25} 1.4430 (the literature gives b. p. 93° and n_D^{25} 1.4456), and a very small amount of 2-bromo-1,1-difluoroethyl acetate, b. p. 60° (60 mm), n_D^{25} 1.4080.

Addition of Bromine to Trifluoroethylene in Acetic Acid

In a similar way, 1.5 liters of trifluoroethylene gave 5 g (50%) of 1,2-dibromo-1,1,2-trifluoroethane, b. p. 72-73° and n_D^{25} 1.410 (the literature gives b. p. 76° and n_D^{25} 1.4191), and a very small amount of 2-bromo-1,1,2-trifluoroethyl acetate, b. p. 46° (35 mm) and n_D^{25} 1.3880.

General Method for the Preparation of Bromo-Acetoxy Addition Compounds of Fluoroolefins

A mixture of 50 ml of glacial acetic acid and 20 g of mercuric acetate or sulfate was prepared in a three-necked flask. The mixture was cooled with ice water and stirred vigorously. Bromine (16 g) was added dropwise, and simultaneously the fluoroolefin was passed so as to decolorize the solution. The precipitate of mercuric bromide was filtered off and washed with water and ether. The filtrate was diluted with 100 ml of ice water, and the organic layer was separated. The acidic aqueous mother liquor was partially neutralized with strong caustic soda solution and extracted with ether. The ether extract was combined with the organic layer, washed with water, with sodium carbonate solution, and again with water, and dried with magnesium sulfate. Ether was removed, and the residue was vacuum distilled. It was found that all operations with di- and tri-fluoroethylenes must be carried out within one day, as otherwise the yields were greatly reduced. Physical and analytical data for the bromoacetoxy compounds that we prepared are given in the table.

Reaction of 1,1-Difluoroethylene with Mercuric Acetate in Glacial Acetic Acid

At room temperature, 2.5 liters of 1,1-difluoroethylene was passed through a vigorously stirred mixture of 25 ml of glacial acetic acid and 10 g of mercuric acetate contained in a three-necked flask. The whole of the mercuric acetate dissolved. The reaction with alkali for mercuric ion was negative. When the solution was cooled a new precipitate formed. It was filtered off, and the filtrate was evaporated to dryness. The yield of (acetoxymercuri)acetic acid was quantitative. The (acetoxymercuri)acetic acid was converted in the usual way into (bromomercuri)acetic acid, m. p. 197° (the literature gives 198°).

Found %: C 6.43; H 0.86.
$C_2H_3O_2HgBr$. Calculated %: C 7.07; H 0.88.

Reaction of 1,1-Difluoroethylene with Mercuric Acetate in Absolute Methanol

Analogous treatment of mercuric acetate with 1,1-difluoroethylene in absolute methanol gave a quantitative yield of methyl (acetoxymercuri)acetate, m. p. 134° (from aqueous alcohol). The melting point of methyl (chloromercuri)acetate was 88° (from aqueous alcohol).

Found %: C 11.68; H 1.69; Cl 12.33.
$C_3H_5O_2HgCl$. Calculated %: C 11.67; H 1.62; Cl 11.82.

Hydrolysis of 2-Bromo-1,1-difluoroethyl Acetate

2-Bromo-1,1-difluoroethyl acetate (4 g) was shaken mechanically with aqueous caustic soda for three hours. The alkaline solution was extracted with ether, acidified with 2 N H_2SO_4, saturated with common salt, and again extracted with ether. The ether extract was dried, and the ether was distilled off. Vacuum distillation of the residue gave acetic acid and bromoacetic acid, b. p. 117° (15 mm) and m. p. 49°.

Neutralization equivalent calculated for $C_2H_3BrO_2$ 139
Value found 140.3.

Hydrolysis of 2-Bromo-1,1,2-trifluoroethyl Acetate

2-Bromo-1,1,2-trifluoroethyl acetate (3 g) was boiled with aqueous caustic soda for 30 minutes. The precipitate formed was filtered off, and to the filtrate, after acidification, a 2% solution of 2,4-dinitrophenylhydrazine in hydrochloric acid was added. The yield of hydrazone was 2 g (80%). After being recrystallized from water, the 2,4-dinitrophenylhydrazone of glyoxylic acid melted with decomposition at 190°.

Found %: C 38.42; H 2.33; N 22.55.
$C_9H_6O_8N_4$. Calculated %: C 37.80; H 2.36; N 22.09.

Reaction of 2-Bromo-1,1-difluoroethyl Acetate with Ethanol

A solution of 10 g of 2-bromo-1,1-difluoroethyl acetate in 7 ml of absolute ethanol was refluxed for 30 minutes. The precipitate was filtered off. A solution of the filtrate in ether was washed with water, with bicarbonate solution, and again with water. The solution was dried, and ether was driven off. Distillation of the residue through a column gave 1.8 g of ethyl acetate and 5.2 g of ethyl bromoacetate, b. p. 155° and n_D^{18} 1.4520 (the literature gives b. p. 159° and n_D^{18} 1.4542).

Synthesis of Bromofluoroacetic Acid

A mixture of 50 ml of water and 20 g of mercuric acetate was stirred at room temperature in a three-necked flask. Bromine (16 g) was added dropwise, and trifluoroethylene (2.5 liters) was passed in simultaneously. The precipitate of mercuric bromide was filtered off. The solution was salted out with common salt and extracted with ether. The ether extract was dried with magnesium sulfate, and the ether was distilled off. Vacuum distillation of the residue gave 4.6 g (30%) of bromofluoroacetic acid, b. p. 103° (20 mm).

Neutralization equivalent calculated for $C_2H_2O_2FBr$ 157
Value found 154

Preparation of 2-Bromo-3,3,3-trifluoro-1-propanol

In a similar way, 30 ml of water, 8 g of bromine, 10 g of mercuric acetate, and 1 liter of 3,3,3-trifluoropropene gave 4.5 g (62%) of 2-bromo-3,3,3-trifluoro-1-propanol, b. p. 34° (12 mm) and 126-127° (760 mm); n_D^{20} 1.4029.

Found %: C 18.66; H 2.43; Br 41.27.
$C_3H_4OF_3Br$. Calculated %: C 18.67; H 2.09; Br 41.41.

The 1-naphthylurethan was prepared with aid of pyridine as catalyst; it melted at 87-88° (the melting point of the 1-naphthylurethan of 3-bromo-1,1,1-trifluoro-2-propanol is 134° [4]).

Found %: C 46.87; H 3.12; N 3.88.
$C_{14}H_{11}F_3Br_3NO_2$. Calculated %: C 46.43; H 3.06; N 3.87.

Preparation of 2,3-Epoxy-1,1,1-trifluoropropane

a) From 2-bromo-3,3,3-trifluoropropyl acetate. 2-Bromo-3,3,3-trifluoropropyl acetate (10 g) was added to a stirred 57% aqueous solution of caustic soda (25 ml) at 100° contained in a three-necked flask. The epoxide was collected in a receiver cooled with a freezing mixture. The yield of aqueous epoxide was 3 g (50%). Water was removed by freezing-out. Fractionation through a column gave a colorless liquid having a very pleasant aromatic odor; b. p. 37-40°; n_D^{20} 1.3050; d_4^{20} 1.382; found MR 15.41; calculated MR 15.97. The literature [4] gives b. p. 39° (748 mm), n_D^{18} 1.2997.

b) From 2-bromo-3,3,3-trifluoro-1-propanol. In a similar way, 6.7 g of 2-bromo-3,3,3-trifluoro-1-propanol gave 0.9 g (26%) of 2,3-epoxy-1,1,1-trifluoropropane.

SUMMARY

1. It was shown that 3,3,3-trifluoropropene, trifluoroethylene, and 1,1-difluoroethylene readily undergo

addition of bromine in glacial acetic acid.

2. For the first time, fluoroolefins were caused to undergo conjugated addition. By the action of bromine on some fluoroolefins in glacial acetic acid, some acetic esters of β-bromo α,α-difluoro alcohols were prepared.

3. It was shown that compounds of this new type have the character of mixed acid anhydrides.

4. By conjugated addition of bromine in water, the bromohydrin of 3,3,3-trifluoropropene was obtained, and this was converted into 2,3-epoxy-1,1,1-trifluoropropane.

5. By conjugated addition of bromine to trifluoroethylene in water, bromofluoroacetic acid was obtained.

6. The addition of mercuric acetate to 1,1-difluoroethylene was effected in acetic acid and in alcohol, the products being the unstable 2-acetoxy-2,2-difluoroethylmercury and 2-ethoxy-2,2-difluoroethylmercury acetates, which are readily transformed into a (halomercuri)acetic acid and its esters.

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DECARBOXYLATION OF α-ACYLAMINO β-HALO CARBOXYLIC ACIDS

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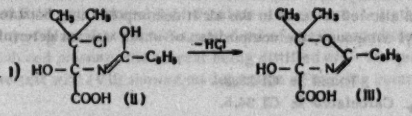
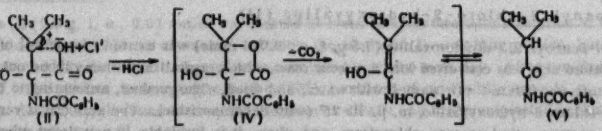
and I. L. Knunyants

It is well known that β-halo acids are readily converted into β-lactones. Thus, at 40-45° sodium 3-bromobutyrate gives the β-lactone in 60-70% yield together with a very small amount of propene [1]. Already at room temperature, salts of 3-bromo-2-methyl- and 3-bromo-2-ethyl-butyric acids form the corresponding lactones, together with olefins and carbon dioxide [2]. There are two different views on the mechanism of the formation of olefins in these and analogous reactions. Erlenmeyer [3] considered that the olefin is formed by decomposition of the intermediately formed β-lactone. It is true that the decomposition of β-lactones into olefins and carbon dioxide is characteristic of these compounds [4], but the conditions necessary are usually more severe than those required for olefin formation from β-bromo acids: under the conditions of the latter reaction, β-lactones usually only undergo hydrolysis with formation of β-hydroxy acids. For this reason, in 1953 Cristol and Norris [5] and, independently, Gravenstein and Lee [6] proposed another mechanism for the formation of olefins from β-halo acids. In a study of the mechanism of the decomposition of salts of α,β-dibromohydrocinnamic acids in aqueous and alcoholic solutions, they concluded that the decarboxylation of α,β-dibromohydrocinnamic acids is accompanied by simultaneous elimination of bromine in the form of an anion.

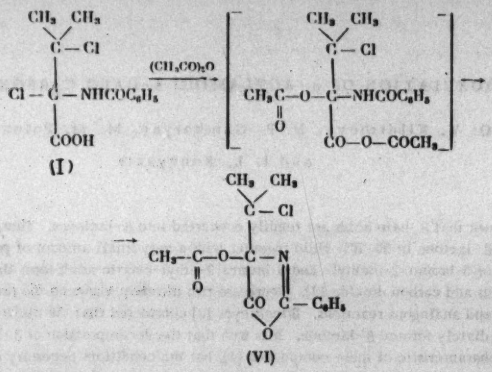
There are no data in the literature on the decarboxylation of N-acyl-2,3-dihaloalanines. Investigation showed that, when treated with water at room temperature, N-benzoyl-2,3-dichlorovaline (I) behaves like N-acyl-2,3-dihaloalanines [7] and is readily converted into N-benzoyl-3-chloro-2-hydroxyvaline (II). Further transformations of this acid under the action of aqueous sodium bicarbonate solution might proceed in two competing directions: with formation of a five-membered oxazoline system (III), and with formation of a four-membered β-lactone system (IV):





N-Acyl-3-halo-2-hydroxyalanines react with aqueous sodium bicarbonate in accordance with the first scheme, the oxazolines formed being hydrolyzed to acyloxypyruvic acids under the conditions of the experiment [7]. N-Benzoyl-3-chloro-2-hydroxyvaline behaves quite differently, and even at room temperature it is very readily decarboxylated with formation of N-isobutyrylbenzamide (V) in 80% yield. It would appear that, in this case, as a result of the presence of two methyl groups on the β-carbon atom, dehydrohalogenation occurs in accordance with the second scheme, the β-lactone (IV) formed being further decomposed into N-isobutyrylbenzamide. The ready decomposition of lactones of this type is confirmed by the recent work of Gresham and coworkers [8].

who showed that isovalerolactone is very unstable, even at room temperature, being decomposed in aqueous solution into isobutene and carbon dioxide. When treated with acetic anhydride or ketene, N-benzoyl-2,3-dichlorovaline and N-benzoyl-3-chloro-2-hydroxyvaline react like their dedimethyl analogs [9] with formation of 4-acetoxy-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one (VI):



The view that replacement of chloro by acetoxy precedes ring closure is confirmed by the fact that no such replacement occurs when 4-chloro-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one (VII) is heated with an equimolecular amount of acetic acid in presence of acetic anhydride.

EXPERIMENTAL

N-Benzoyl-2,3-dichlorovaline (I)

2-Benzamido-3-methylcrotonic acid (11 g, i. e., 0.05 mole) was treated with excess of chlorine dissolved in carbon tetrachloride (7.1 g of chlorine in 71 ml of carbon tetrachloride). Reaction proceeded with evolution of heat. After one day the precipitate was filtered off, washed with carbon tetrachloride, and dried. The product, amounting to 13.4 g (93%), was N-benzoyl-2,3-dichlorovaline, obtained in the form of colorless crystals, m. p. 104° (with decomposition). When allowed to stand in the air it decomposed into benzamide, hydrogen chloride, isobutyric acid, and a carbonyl compound, the composition of which was not determined.

Found %: Cl 23.3.
$C_{12}H_{13}NO_3Cl_2$. Calculated %: Cl 24.5.

N-Benzoyl-3-chloro-2-hydroxyvaline (II)

N-Benzoyl-2,3-dichlorovaline (7.5 g, i. e., 0.026 mole) was treated with 30 ml of water. After some time the dichloro acid was converted into a viscous mass, which crystallized when rubbed out. After two hours the precipitate was filtered off, washed with water, and dried. The product, amounting to 5.1 g (73%), was N-benzoyl-3-chloro-2-hydroxyvaline, m. p. 70-75° (with decomposition). The acid (II) is very readily soluble in alcohols, acetone, ethyl acetate, chloroform, and ether; it is insoluble in petroleum ether. N-Benzoyl-3-chloro-2-hydroxyvaline is more stable than N-benzoyl-2,3-dichlorovaline, but it decomposes into the same products when allowed to stand in the air.

Found %: Cl 13.0.
$C_{12}H_{14}NO_4Cl$. Calculated %: Cl 13.1.

4-Acetoxy-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one (VI)

a) A mixture of 5.8 g (0.02 mole) of (I), 50 ml of acetic anhydride, and 25 ml of carbon tetrachloride was heated under reduced pressure at 70-80°. The crystalline precipitate was filtered off and washed with a little absolute alcohol. The yield of (VI), m. p. 95° (from absolute alcohol), was 3.8 g (65%). This substance is very readily soluble in ether, chloroform, acetone, and dioxane; it can be crystallized from ethanol and acetic anhydride.

Found %: C 57.12; H 5.00; N 4.77; Cl 11.85.
$C_{14}H_{14}NO_4Cl$. Calculated %: C 57.0; H 4.75; N 4.75; Cl 12.00.

4-Acetoxy-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one remains practically unchanged when heated for a long time with acetic anhydride and acetic acid or with methanol containing a catalytic amount of potassium carbonate. In presence of an equimolecular amount of potassium carbonate, however, (VI) is immediately decomposed; even at room temperature, with formation of acetic acid, benzamide, and a carbonyl compound of undetermined composition. The substance (VI) may be preserved in the open for several months, but it decomposes in a sealed tube.

b) Ketene was passed into a suspension of 1.45 g (0.005 mole) of (I) in 20 ml of absolute benzene until solution was complete. The solution was evaporated at room temperature under reduced pressure, and the crystals precipitated were filtered off. The yield of white crystals of (VI), m. p. 94-95°, was 0.4 g (29%). The filtrate was treated with sodium bicarbonate, and crystals of m. p. 155°, identified as N-isobutyrylbenzamide (see below), were isolated.

c) A mixture of 2.4 g (0.0088 mole) of (II), 25 ml of acetic anhydride, and 20 ml of carbon tetrachloride was heated under reduced pressure at 70-80°. The crystalline precipitate was filtered off and washed with a little absolute alcohol. The yield of white crystals of (VI), m. p. 95°, was 0.95 g (40%).

4-Chloro-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one (VII)

A mixture of 2.9 g (0.01 mole) of N-benzoyl-2,3-dichlorovaline, 2.1 g (0.01 mole) of phosphorus pentachloride, and 20 ml of absolute benzene was heated for two hours. It was then evaporated to dryness under reduced pressure, and the residue was crystallized from petroleum ether. The product, amounting to 2 g (72%), was (VII), obtained in the form of colorless crystals, m. p. 60-64° (with decomposition). This substance is very soluble in the usual organic solvents. It is decomposed when allowed to stand in the air for a few hours.

Found %: Cl 25.25.
$C_{13}H_{11}NO_4Cl_2$. Calculated %: Cl 26.10.

A mixture of 0.55 g (0.002 mole) of 4-chloro-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one, 0.12 g (0.002 mole) of glacial acetic acid, and 5 ml of acetic anhydride in 5 ml of carbon tetrachloride was heated at 70-80° under reduced pressure, the solvent being distilled off. The product (0.5 g) consisted of crystals of m. p. 60-64°. A mixture test with (VII) showed no depression of melting point.

N-Isobutyrylbenzamide (V)

a) The substance (I) (2.9 g, i. e., 0.01 mole) was treated at room temperature with a solution of 0.85 g (0.01 mole) of sodium bicarbonate in 10 ml of water*. Almost the whole of (I) went into solution, but crystals then began to be precipitated. Evolution of carbon dioxide continued until the next day. After two days the precipitate was filtered off. The product, amounting to 0.46 g (77%), consisted of snow-white crystals, m. p. 155° (from absolute alcohol). N-Isobutyrylbenzamide readily dissolves in alkalis and is reprecipitated unchanged when the solution is carefully acidified.

Found %: C 68.95; H 6.98; N 7.57.
$C_{11}H_{13}NO_2$. Calculated %: C 69.20; H 6.80; N 7.35.

N-Isobutyrylbenzamide (0.95 g, i. e. 0.005 mole) was boiled for 30 minutes with a solution of 1 g of potas-

* The reaction is more rapid in presence of a large amount of bicarbonate, but the yield of N-isobutyrylbenzamide is not increased.

sium hydroxide in 10 ml of water. The solution was neutralized with sulfuric acid, and the precipitate formed was filtered off. The product, amounting to 0.19 g (80%), consisted of crystals which melted at 121° after recrystallization from water. A mixture with known benzoic acid showed no depression of melting point. A volatile acid was steam-distilled from the filtrate, 0.0047 mole (93%) being obtained. The solution of the acid was neutralized with caustic soda and evaporated, and the salt that remained was treated with thionyl chloride and aniline. Clear crystals of m. p. 104° (from aqueous alcohol) were obtained. A mixture with isobutyranilide melted at the same temperature.

b) The substance (II) (1.37 g, i. e., 0.005 mole) was treated with a solution of 0.42 g (0.005 mole) of sodium bicarbonate in 5 ml of water. After two days 0.75 g (81%) of N-isobutyrylbenzamide, m. p. 155°, was filtered off.

c) The substance (II) (1.37 g, i. e., 0.005 mole) was treated with 10 ml of water. After ten days 0.82 g (86%) of N-isobutyrylbenzamide, m. p. 155°, was filtered off. A mixture with a sample from experiment (a) melted at the same temperature.

d) The substance (VII) (1.37 g, i. e., 0.005 mole) was left in the air for one day. The resulting oil was treated with sodium bicarbonate solution. After two days 0.67 g (70%) of N-isobutyrylbenzamide crystals, m. p. 155°, were filtered off.

SUMMARY

1. It was shown that N-benzoyl-3-chloro-2-hydroxyvaline is readily decarboxylated with formation of N-isobutyrylbenzamide.

2. 4-Chloro-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one and 4-acetoxy-4-(1-chloro-1-methylethyl)-2-phenyl-2-oxazolin-5-one were prepared for the first time.

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* T.p. = C. B. Translation pagination.

SOME CONDENSATIONS OF ALIPHATIC NITRO CARBOXYLIC ESTERS*

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In a previous communication [1] we showed that, under certain conditions, nitroacetic ester condenses with aliphatic aldehydes with formation of β-hydroxy α-nitro carboxylic esters. Also, nitroacetic ester was cyanoethylated, and the mono- and bis-2-cyanoethyl derivatives were isolated. The biscyanoethyl derivative was converted into the corresponding tricarboxylic ester. In the present investigation we made a more detailed study of the transformations which can be undergone by condensation products of nitroacetic ester, and we also extended these condensation reactions to 3-nitropropionic and 4-nitrobutyric esters.

We found previously that 3-hydroxy-2-nitrobutyric ester, obtained by the condensation of nitroacetic ester with acetaldehyde, boils over a fairly wide range. We suggested that in this reaction two diastereoisomeric forms were obtained. In the hope of separating the isomers, we have vacuum distilled the product through a column having a filling of annealed nichrome spirals. Two fractions were obtained: the first was the dehydration product of the hydroxy nitro ester, i. e., 2-nitrocrotonic ester, and the second was hydroxynitrobutyric ester:

$$CH_3CHCHCOOC_2H_5 \rightarrow CH_3CH=CCOOC_2H_5.$$
$$\quad\;\; |\quad\;\; | \qquad\qquad\qquad\quad\;\; |$$
$$\quad HO\;\; NO_2 \qquad\qquad\qquad\quad NO_2$$

However, the occurrence of this partial dehydration of the hydroxy nitro ester leaves the question of the presence of two diastereoisomeric forms in the product open. The view that two such forms are present is supported by the fact that the products obtained by distillation in the ordinary way have varying refractive indices and densities, but constant molecular weight and composition. Partial dehydration during distillation can be explained by a greater tendency in one of the diastereoisomeric forms to undergo dehydration.

As attempts to obtain a crystalline derivative of 3-hydroxy-2-nitrobutyric ester were not successful, we had recourse to its reactions. Egorov [2] reduced the product of the addition of oxides of nitrogen to crotonic ester with tin and hydrochloric acid and obtained threonine. We attempted to hydrogenate 3-hydroxy-2-nitrobutyric ester catalytically. Hydrogenation without addition of acid gave an amine of composition $C_8H_{15}O_2N$, which we did not investigate further. When oxalic acid was added to the reaction mixture, two crystalline products were isolated. One of these corresponded in analysis to the monohydrate of ammonium hydrogen oxalate, and the other to the oxalate of the ethyl ester of threonine:

$$CH_3CH-CHCOOC_2H_5 \rightarrow CH_3CH-CHCOOC_2H_5 + C_2O_4H_4\cdot NH_3\cdot H_2O.$$
$$\quad\;\; |\quad\;\; | \qquad\qquad\quad\;\; |\quad\;\; |$$
$$\quad HO\quad NO_2 \qquad\qquad\quad HO\quad NH_2C_2O_4H_2$$

For neither product did the yield exceed 30%.

We then hydrogenated the monocyanoethyl derivative of nitroacetic ester in the hope of obtaining arginine, but under our conditions of reaction (pyridine was used as solvent) the nitro group was only partially reduced (to the nitroso stage). The product – the oxime of 4-cyano-2-oxobutyric ester – was isolated as the O-benzoyl derivative. This substance did not dissolve in alkalis in the cold, but it dissolved at a higher temperature with

* This paper forms part of a thesis for a candidates's diploma and describes work carried out under the supervision of Academician V. M. Rodionov.

evolution of ammonia; when the solution was acidified, benzoic acid was liberated.

$$NCCH_2CH_2CHCOOC_2H_5 \xrightarrow[Pd]{H_2} NCCH_2CH_2CCOOC_2H_5.$$
$$\quad NO_2 \qquad\qquad\qquad\quad NOCOC_6H_5$$

When biscyanoethylated nitroacetic ester was hydrolyzed with aqueous-alcoholic caustic soda, simultaneous decarboxylation occurred with formation of 4-nitropimelonitrile in 78% yield. This substance was obtained by Buckley [3] in very poor yield by the cyanoethylation of nitromethane, taken in large excess.

It was of interest to investigate the effect of increasing the distance between the nitro group and the ester grouping on the ease of reaction and the nature of the products. With this object we synthesized the methyl esters of 3-nitropropionic and 4-nitrobutyric acids. The first of these, like 3-nitropropionic esters in general, has not been described before. There are instructions for the preparation of the ethyl ester in a paper by Lewkowitsch [4], who distilled the products of reaction between 3-iodopropionic ester and silver nitrite and obtained two fractions: one boiling at 161-165° and one boiling over the range 200-230°. He took the first fraction to be the required 3-nitropropionic acid, and the second he did not investigate further.

Our attempts to reproduce Lewkowitsch's results were unsuccessful. The first fraction was obtained in very small amount, and its boiling point was 15° higher than that given by Lewkowitsch; it readily decomposed with evolution of oxides of nitrogen. When we vacuum distilled the reaction product, we obtained two fractions. The first fraction, b. p. 26-27° (2 mm) had a strong odor of oxides of nitrogen; the second boiled at 73-74° (2 mm). At atmospheric pressure the second fraction boiled with decomposition at above 220°.

Boiling point tables [5] indicate that the first fraction, which corresponds to the substance that Lewkowitsch regarded as nitropropionic ester, is nitrous ester. The second, high-boiling fraction, which corresponds to the substance that he did not investigate, was in fact the desired product. We found that the same results were obtained when the iodo derivative was replaced by the more readily available bromo derivative:

$$BrCH_2CH_2COOCH_3 \xrightarrow{AgNO_2} O_2NCH_2CH_2COOCH_3$$

The performance of the Meyer reaction was greatly simplified by dilution of the reaction mixture with benzene or acetonitrile. In this way we prepared methyl 3-nitropropionate in 70% yield.

The recent paper by Treibs and Reinheckel [6] contains some very doubtful data on the preparation of 3-nitropropionic ester: they obtained a product of doubtful purity – no constants are given – by treating the monoethyl ester of bromosuccinic acid with sodium nitrite, and they took it to be 3-nitropropionic ester because they obtained a very small yield of β-alanine hydrochloride when they reduced it. We tried to prepare 3-nitropropionic acid by the hydrolysis and decarboxylation of the 1-nitro-1,1,2-ethanetricarboxylic ester that we had prepared previously, but treatment with concentrated hydrochloric acid at 100° did not affect it, and treatment with this acid at the boil decomposed it completely. β-Nitro carboxylic acids are extremely stable to the action of alkalis.

The condensation of methyl 3-nitropropionate with acetaldehyde was carried out by warming the reactants in presence of potassium carbonate. The product was methyl 4-hydroxy-3-nitrovalerate. No product of higher boiling point – a dihydroxy or dinitro compound – was formed in appreciable amount. The high boiling point of this compound – 133° (2 mm) – is noteworthy: the isomeric ethyl 3-hydroxy-2-nitrobutyrate boils at about 90° at the same pressure.

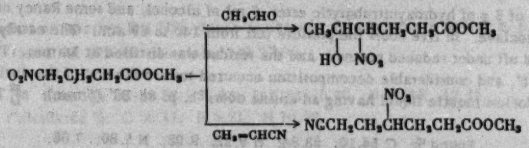
$$O_2NCH_2CH_2COOCH_3 \xrightarrow{CH_3CHO} CH_3CHCHCH_2COOCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad HO \quad NO_2$$
$$O_2NCH_2CH_2COOCH_3 \xrightarrow{CH_2=CHCN} NCCH_2CH_2CHCH_2COOCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

The condensation of 3-nitropropionic ester with acrylonitrile proceeded considerably more readily than

that of nitroacetic ester. In presence of Rodionov's catalyst, an exothermic reaction occurred already at room temperature, and we obtained methyl 5-cyano-3-nitrovalerate together with some unchanged nitropropionic ester. Some noncrystallizing viscous oil remained as a residue from the distillation.

The acetaldehyde and acrylonitrile condensation reactions were extended also to 4-nitrobutyric ester. This has been prepared previously by Leonard and Beck [7] by the condensation of an excess of nitromethane with methyl acrylate in presence of a solution of Triton B in tert-butyl alcohol. As Triton B was not available, we used a solution of trimethylphenylammonium ethoxide in ethanol and obtained the desired substance in 20-22% yield. Appreciable amounts of dimethyl 4-nitropimelate were obtained at the same time.

Reaction of 4-nitrobutyric ester with acetaldehyde proceeded readily at room temperature in presence of an anion-exchange resin (Anionite). The condensation did not proceed so readily in presence of potassium carbonate. In both cases the product was methyl 5-hydroxy-4-nitrohexanoate:



The cyanoethylation of 4-nitrobutyric ester proceeded very readily in the cold, even in the presence of sodium methoxide, and the product was methyl 6-cyano-4-nitrohexanoate. The cyanoethylation of nitroacetic ester does not go in presence of sodium methoxide, even when heat is applied.

EXPERIMENTAL

2-Nitrocrontic Ester

The product obtained by the condensation of nitroacetic ester with acetaldehyde [1], which boiled over a range of 20°, was fractionated through a 30-cm column filled with nichrome spirals. At 5 mm two fractions were obtained, and after redistillation from an ordinary Claisen flask these gave the following results:

Fraction I, b. p. 81.5-82° (4 mm); n_D^{20} 1.4498; d_4^{20} 1.1469; weight 10 g; 2-nitrocrotonic ester.

Found %: C 44.99; 45.22; H 5.48; 5.34; N 8.37; 8.57.
$C_4H_5O_4N$. Calculated %: C 45.28; H 5.66; N 8.81.

Found M: 159.5; 157.1 (cryoscopically in benzene).
Calculated M: 159.

Fraction II, b. p. 89-91° (4 mm); n_D^{20} 1.4392; weight 8 g; 3-hydroxy-2-nitrobutyric ester.

Found M: 175.1; 175.9 (cryoscopically in benzene).
$C_4H_{11}O_5N$. Calculated M: 177.16.

Residue in flask and entrapment, 5.7 g; b. p. 91.5-92.5° (4 mm); n_D^{20} 1.4350; d_4^{20} 1.1262.

Hydrogenation of 3-Hydroxy-2-nitrobutyric Ester

1. A mixture of 3.5 g of the nitro compound, 2.5 g of crystalline oxalic acid, 3.5 g of palladium catalyst (5% Pd on $BaSO_4$), and 10 ml of dioxane was prepared in a 50-ml shaking autoclave. In two hours at room temperature the hydrogen pressure fell from 127 to 70 atm, and after 20 hours the pressure was 67 atm. The catalyst was filtered off and washed with dioxane. The filtrate was evaporated down as far as possible on a water bath. The thick yellow oily residue was dissolved in 10 ml of 2-butanone, and the solution was cooled in an ice bath. Rubbing with a glass rod caused a precipitate to form. It was filtered off and washed with ether; it then weighed 3 g. The product was found to be a mixture of approximately equal amounts of two substances. One substance was soluble in hot 2-butanone, and the other was insoluble. After three recrystallizations from 2-butanone the

soluble part was obtained in the form of a white powder. This sintered at 82°, became clear at 106-107°, and formed a sharp meniscus at 111-112°. It was found to be the oxalate of the ethyl ester of threonine.

Found %: C 40.83; 40.90; H 6.40; 6.37; N 6.02; 5.93.
$C_6H_{13}O_5N$. Calculated %: C 40.52; H 6.33; N 5.91.

The part that was insoluble in 2-butanone was recrystallized from a 1:1 mixture of water and 2-butanone. It sintered at 201° and melted at 205-206° (with decomposition). It was found to be the monohydrate of ammonium hydrogen oxalate.

Found %: C 19.01; 19.17; H 6.60; 5.54; N 10.87; 10.67
$C_2H_7O_5N$. Calculated %: C 19.2; H 5.6; N 11.2.

2. A mixture of 8 g of hydroxynitrobutyric ester, 6 ml of alcohol, and some Raney nickel was prepared in a 50-ml shaking autoclave. In five hours the pressure fell from 140 to 89 atm. The catalyst was filtered off, alcohol was distilled off under reduced pressure, and the residue was distilled at 14 mm. The product (2 g) boiled over the range 75-95°, and considerable decomposition occurred toward the end of the distillation. Redistillation gave 0.76 g of a colorless mobile liquid having an amine odor: b. p. 88-89° (5 mm); n_D^{20} 1.4337; d_4^{20} 0.9955.

Found %: C 54.10; 53.84; H 9.22; 9.23; N 7.80; 7.66.

The analytical data correspond to $C_8H_{15}O_3N$. The compound was not investigated further.

Hydrogenation of (2-Cyanoethyl)nitroacetic [4-Cyano-2-nitrobutyric] Ester

A mixture of 5 g (0.027 mole) of the nitro compound, 10 ml of dry pyridine, and 1 g of Pd-$BaSO_4$ (5%) was prepared in a 50-ml shaking autoclave. The autoclave was shaken at room temperature for seven hours and then heated by passage of steam through the sleeve until the pressure ceased to fall (one hour). The catalyst was filtered off and washed with pyridine. The pyridine solution was cooled in an ice-salt mixture, and 7.5 g (0.054 mole) of benzoyl chloride was added a little at a time. The mixture was warmed to room temperature, 40 ml of water and 20 ml of alcohol were added, and the mixture was heated to 60°. After being cooled to 0° and rubbed with a glass rod, the precipitated oil solidified and formed brown flocs. It was filtered off and washed twice with cooled dilute alcohol. The product was 4.1 g of colorless crystals, and 3.2 g (0.026 mole) of benzoic acid was isolated from the filtrate. The product was recrystallized twice from 60% alcohol, and it then melted at 95.5-96.5°. It was found to be the O-benzoyl derivative of the oxime of ethyl 4-cyano-2-oxobutyrate.

Found %: C 61.40; 61.34; H 5.22; 5.07; N 10.35; 10.43.
$C_{14}H_{14}N_2O_4$. Calculated %: C 61.4; H 5.13; N 10.22.

4-Nitropimelonitrile

(Bis-2-cyanoethyl)nitroacetic ester [4-cyano-2-(2-cyanoethyl)-2-nitrobutyric ester] (12 g, i. e., 0.05 mole) was warmed with 40 ml of alcohol until dissolved. An oil separated when the solution was cooled, and a solution of 2.2 g (0.055 mole) of caustic soda in aqueous alcohol was added to this mixture. The temperature rose a little, and a precipitate then formed. The mixture was heated for a few minutes in a water bath. When the amount of precipitate ceased to increase, it was filtered off. The solution was set aside at room temperature for two days. The small amount of precipitate that formed during this time was separated, and the solution was acidified to litmus with dilute hydrochloric acid, cooling being applied. Rubbing with a rod caused a precipitate to appear, and this was filtered off and washed with cold methanol; weight 4.8 g. By successive evaporations, a further 1.7 g of pure product and 0.5 g of impure product was obtained from the mother liquor. The total yield of pure product was 6.5 g, i. e., 0.039 mole (78%). It formed long colorless needles, m. p. 64.6-64.9° (from alcohol in presence of activated charcoal). The literature [3] gives m. p. 63°.

Found %: C 50.27; 50.39; H 5.65; 5.61; N 25.29; 25.59.
$C_7H_9N_3O_2$. Calculated %: C 50.2; H 5.39; N 25.2.

Methyl 3-Nitropropionate

1. Methyl 3-bromopropionate (10 g, i. e., 0.06 mole) was mixed with a few grams of sand in a 50-ml flask fitted with a stirrer having a rubber seal. An addition was made of 10 g (0.065 mole) of dry silver nitrite that had been recrystallized from water. Under stirring and periodic shaking, the almost dry mixture was heated at 60-65° in a water bath. After 90 minutes all the nitrite had settled on the bottom and formed a thick slurry, which could still be stirred, however. After two hours the mixture had thickened to such an extent that it could no longer be stirred. It was heated for a further 30 minutes and then cooled. It was mixed with ether, and the precipitate was filtered off and washed twice with ether. The ether solution was dried with calcium chloride. Ether was distilled off, and the residue was distilled at a residual pressure of 2 mm. Two fractions were obtained:

Fraction I, b. p. 26-27°; 1.9 g
Fraction II, b. p. 73-74°; 4.0 g.

After redistillation of Fraction II a 50% yield was obtained of a substance having b. p. 68° (1 mm); n_D^{20} 1.4350; d_4^{20} 1.2486; found MR 27.86; calculated MR 27.95.

Found %: C 36.33; 36.04; H 5.54; 5.43; N 10.45; 10.61.
$C_4H_7O_4N$. Calculated %: C 36.11; H 5.21; N 10.52.

2. A mixture of 30 g (0.18 mole) of methyl 3-bromopropionate, 30 g (0.195 mole) of silver nitrite, and 30 ml of dry benzene was heated, as above, with exclusion of air for 15 hours at 58°. The precipitate was filtered off, and the filtrate was heated with 9.5 g of fresh silver nitrite for ten hours. The mixture was filtered, benzene was distilled off at the pump, and the product was again filtered and was vacuum distilled. The yield of methyl 3-nitropropionate was 16.7 g (70%).

Methyl 4-Hydroxy-3-nitrovalerate

3-Nitropropionic ester (4 g, i. e., 0.03 mole) was dissolved in 5 ml of ethanol. Acetaldehyde (4 ml) and an aqueous solution of 0.1 g of potassium carbonate were added at 10°. The mixture was diluted with water until a homogeneous solution was obtained. A further 3.5 ml of acetaldehyde was added at room temperature, and the mixture was heated for ten minutes in a water bath at 50°. The mixture was cooled, and an equal volume of ethylene dichloride was added. The aqueous layer was separated, and the organic layer was washed again with water. Solvent was distilled off, and distillation of the residue at 2 mm gave 3.0 g (57%) of product, b. p. 122-135° (only a few drops distilled above this range). A second distillation gave a colorless oil, b. p. 133° (2 mm); n_D^{20} 1.4608; d_4^{20} 1.2579.

Found %: C 40.96; 41.03; H 6.20; 6.36; N 7.96; 8.07.
$C_6H_{11}O_5N$. Calculated %: C 40.67; H 6.26; N 7.90.

Methyl 5-Cyano-3-nitrovalerate

A mixture of 4 g (0.03 mole) of 3-nitropropionic ester and 1.7 g (0.032 mole) of acrylonitrile was prepared, and a catalyst prepared by the decomposition of 0.5 g of trimethylphenylammonium benzenesulfonate with the theoretical amount of sodium ethoxide [1] was added. Heat was evolved. The mixture was cooled and acidified with concentrated hydrochloric acid. An equal volume of ethylene dichloride was added. The organic layer was washed with water, solvent was distilled off, and the residue was distilled at 1 mm. Unchanged reactants were distilled off below 100° (2.7 g). The cyanoethyl derivative (0.5 g) came over at 162-170° (1 mm); n_D^{23} 1.4638.

Found %: N 15.32; 15.30.
$C_7H_{10}O_4N_2$. Calculated %: N 15.05.

Methyl 5-Hydroxy-4-nitrohexanoate

1. A mixture of 1.5 g of 4-nitrobutyric ester, 6 g of 40% alcoholic acetaldehyde, and a solution of 0.1 g of potassium carbonate in 5 ml of water and 2 ml of alcohol was set aside overnight. The mixture was then heated for one hour at 50°. It was cooled, acidified with dilute (1:1) sulfuric acid, and extracted with ether. The ether

layer was washed with water, dried with anhydrous sodium sulfate, and distilled, the residue after removal of ether being distilled at 3 mm. The product, amounting to 0.62 g, had b. p. 135-137° and n_D^{20} 1.4777.

2. A mixture of 2 g of 4-nitrobutyric ester, 10 g of 40% methanolic acetaldehyde, and 0.5 g of Anionite was shaken for six hours. The mixture was set aside overnight. The catalyst was filtered off and washed with ether, the washings being added to the reaction mixture. The lower-boiling fractions were distilled off, and the residue was distilled at 2 mm. The product (1.2 g) had b. p. 133-135° and n_D^{20} 1.4778.

The products of the two experiments were combined and found to have a density of d_4^{20} 1.0811.

Found %: N 7.95; 7.38.
$C_7H_{13}O_5N$. Calculated %: N 7.35.

Methyl 6-Cyano-4-nitrohexanoate

A mixture of 5 g (0.034 mole) of 4-nitrobutyric ester and 2 g (0.06 mole) of acrylonitrile was cooled to 0°, and a solution of sodium (a piece about as big as a lentil) in 3 ml of methanol was added. It was necessary to cool periodically with ice water in order to maintain the temperature of the mixture below 25°. The mixture was set aside at room temperature for several hours and then acidified with concentrated hydrochloric acid. An equal amount of ethylene dichloride was added, the organic layer was washed with water, and the solvent was distilled off. Vacuum distillation of the residue gave 2.1 g of product boiling at 166-174° (2 mm). For the purpose of analysis the substance was redistilled, and a sample of b. p. 161-163° (1 mm) had the following constants: n_D^{20} 1.4588 and d_4^{20} 1.1901. This sample gave a qualitative reaction for a secondary nitro compound.

Found %: N 13.82; 13.74.
$C_8H_{12}O_4N$. Calculated %: N 14.00.

1-Nitro-1,1,2-ethanetricarboxylic Ester

A mixture of 50 g of fuming nitric acid and 40 g of acetic anhydride was heated to 50°, and 36 g of triethyl 1,1,2-ethanetricarboyxlate was added dropwise. The temperature of the reaction mixture was maintained in the range 45-50° by external cooling. After the whole of the ester had been added, the mixture was set aside until heat ceased to be evolved and was then poured into 1 liter of cold water. After 90 minutes the oil that had separated was extracted with ether. The ether solution was washed with sodium carbonate solution and then with sodium chloride solution; it was dried with sodium sulfate. The volatile components were evaporated off at the pump. The residue was 39 g of a colorless oil, which could not be distilled without decomposition.

This product (30 g) was heated with 100 ml of concentrated hydrochloric acid in a water bath until gas ceased to be evolved (1 hour). The oil remaining at the bottom was extracted with ether, the ether solution was dried with calcium chloride, and ether was distilled off. Vacuum distillation of the residue gave 9 g of a product boiling over the range 149-152° (1.5 mm). A fraction taken in the range 150-151° (1.5 mm) had d_4^{20} 1.2068 and n_D^{20} 1.4450; a thick colorless odorless oil.

Found %: C 44.91; 45.06; H 5.85; 5.93; N 5.00; 5.14.
$C_{11}H_{17}O_8N$. Calculated %: C 45.36; H 5.84; N 4.81.

SUMMARY

1. It was found that partial dehydration occurred when ethyl 3-hydroxy-2-nitrobutyrate was distilled.

2. The hydrogenation of 3-hydroxy-2-nitrobutyric ester and of monocyanoethylated nitroacetic ester was studied. Biscyanoethylated nitroacetic ester, subjected to hydrolysis and then decarboxylation, gave 4-nitropimelonitrile in 78% yield.

3. Methyl 3-nitropropionate was prepared in 50-70% yield from 3-bromopropionic ester by Meyer's reaction.

4. The condensation products formed by acetaldehyde and by acrylonitrile with methyl 3-nitropropionate and with methyl 4-nitrobutyrate were prepared.

5. Triethyl 1-nitro-1,1,2-ethanetricarboxylate was prepared by the nitration of triethyl 1,1,2-ethanetricarboxylate.

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PRIMARY RADICAL FORMATION IN THE VAPOR-PHASE NITRATION OF ALKANES WITH NITROGEN DIOXIDE

A. V. Topchiev and N. N. Kaptsov

In order to explain the vapor-phase nitration of alkanes by nitric acid, the following radical mechanism has been assumed in the literature [1-3]:

$$HONO_2 \rightarrow OH + NO_2. \quad (1)$$
$$RH + OH \rightarrow R + H_2O. \quad (2)$$
$$R + HONO_2 \rightarrow RNO_2 + OH. \quad (3)$$
$$OH + RH \rightarrow R + H_2O \text{ etc.} \quad (4)$$
$$R + NO_2 \rightarrow RNO_2. \quad (5)$$

This mechanism comprises Reactions (1), (2), (3), and (4), in which free alkyl and hydroxyl radicals are formed, and Reaction (5), in which alkyl radical combines with the monomeric form of nitrogen dioxide. This last reaction is the fundamental elementary act in the formation of nitroalkanes.

It is considered [4-6] that, when nitrogen dioxide is used as nitrating agent, free-radical formation occurs by reaction between radical-like [6, 7] nitrogen dioxide and the alkane in accordance with the equation:

$$RH + NO_2 \rightarrow R + HNO_2. \quad (6)$$

According to Titov [4, 8], Reaction (6) is the main source of alkyl radicals, even in the vapor-phase nitration of alkanes with nitric acid, the latter compound then serving only as a source of nitrogen dioxide and as a means of regenerating it from lower nitrogen oxides. In the gas phase the probability of the occurrence of the elementary act is identical for all molecules [9], and all NO_2 molecules have radical properties in equal measure; it may therefore be assumed that the elementary process (6) takes place on the scale of a macro system consisting of nitrogen dioxide and hydrocarbon molecules.

It would appear possible, therefore, to estimate the probability of the formation of alkyl radicals in the reaction of nitrogen dioxide with alkanes from the change in free energy. The temperature dependence of free energy for the vapor-phase nitration of methane and ethane with nitric acid is given in the literature [10]:

$$CH_4(g) + HNO_3(g) = CH_3NO_2(g) + H_2O(g). \quad (7)$$
$$\Delta Z^\circ_T = -25975 - 5.76\,T. \quad (8)$$
$$C_2H_6(g) + HNO_3(g) = C_2H_5NO_2(g) + H_2O(g). \quad (9)$$
$$\Delta Z^\circ_T = -28050 - 3.15\,T. \quad (10)$$

For the vapor-phase nitration of cyclohexane with nitrogen dioxide in accordance with the equation:

$$C_6H_{12} + 1.5\ NO_2 = C_6H_{11}NO_2 + 0.5\ NO + 0.5\ H_2O \quad (11)$$

the temperature-dependence of ΔZ°_T is obtained [11], by the substitution of known values of ΔZ°_T in suitable thermodynamic expressions, in the form of the equation:

$$\Delta Z^\circ_T = -22055 - 3.65\,T \ln T + 5.03 \cdot 10^{-3} T^2 - 0.65 \cdot 10^{-6} T^3 + 0.34\,T, \quad (12)$$

which may be reduced to the linear form:

$$\Delta Z^{\circ}_{T} = -21560 - 18.35\,T. \qquad (13)$$

The above-cited relationships between ΔZ°_{T} and temperature show that at all temperatures the nitration reactions of hydrocarbons in the vapor phase are spontaneous processes, i.e., proceed with reduction in free energy, when nitric acid or oxides of nitrogen are used as nitrating agent. Hence, the intermediate stages of the reaction (regarded from the macroscopic point of view) must also be thermodynamically possible.

Heat Contents and Free Energies of Formation of Some Aliphatic Radicals [14]

Radical	$\Delta H^{\circ}_{298.2}$ (cal/mole)	$\Delta Z^{\circ}_{298.16}$ (cal/mole)
CH_3	32022	32600
C_2H_5	25175	31600
C_3H_7	18091	32100
CH_3 / $CH-$ / CH_3	12100	26200
C_4H_9	12099	32700
C_5H_{11}	6411	34000
C_6H_{13}	1151	35700
C_7H_{15}	−3775	37000
C_8H_{17}	−8701	39800

For the reaction

$$CH_4(g) + NO_2(g) \longrightarrow CH_3(g) + HNO_2(g) \qquad (14)$$

we have [12]:

$\Delta Z^{\circ}_{298}CH_4 = -12.14$ kcal/mole.
$\Delta Z^{\circ}_{298}NO_2 = 12.26$ kcal/mole.
$\Delta Z^{\circ}_{298}CH_3 = 31.5$ kcal/mole.
$\Delta Z^{\circ}_{298}HNO_2 = -4.8$ kcal/mole.

The free energy of formation of gaseous nitrous acid is found from the standard entropy, as given by spectroscopic data [13]:

$S^{\circ}_{298}HNO_2(g) = 56$ entropy units

and from its heat of formation, which is easily found to be 14.2 kcal from the following thermodynamic equations:

$$H_2 + \tfrac{1}{2}O_2 = H_2O(g) + 57.8 \text{ kcal.} \qquad (15)$$

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 = NO(g) - 21.5 \text{ kcal.} \qquad (16)$$

$$\tfrac{1}{2}N_2 + O_2 = NO_2(g) - 7.96 \text{ kcal.} \qquad (17)$$

Hence, for reaction of methane with nitrogen dioxide (Equation 14) we have:

$$\Delta Z^{\circ}_{298} = 31.5 - 4.8 + 12.14 - 12.26 = 26.6 \text{ kcal.}$$

The value of ΔZ° obtained indicates a very low probability for the formation of methyl radicals in reaction between NO_2 and CH_4 in accordance with Equation 14. Similar conclusions follow also for reactions of nitrogen dioxide with other alkanes. The values of ΔZ°_{298} for various radicals are given in the table.

As the reactions of alkanes with nitrogen dioxide in accordance with Equation 6 are all of one type, then according to Kireev [15, 16] the following relationship holds:

$$\Delta H^{\circ}_1 - \Delta H^{\circ}_2 = \Delta Z^{\circ}_1 - \Delta Z^{\circ}_2, \qquad (18)$$

in which ΔH°_1, ΔZ°_1, ΔH°_2, and ΔZ°_2 are the heat-content and free-energy changes for two of these reactions.

On the basis of this relationship, for the reaction between ethane and nitrogen dioxide in accordance with the equation:

$$C_2H_6 + NO_2 \rightarrow C_2H_5 + HNO_2$$

the change of free energy is

$$\Delta Z_2^\circ = \Delta Z_1^\circ + (\Delta H^\circ_{C_2H_5} - \Delta H^\circ_{CH_3}) + (\Delta H^\circ_{CH_4} - \Delta H^\circ_{C_2H_6}), \quad (19)$$

in which ΔZ_1° = 26.6 kcal, the standard free-energy change for the reaction of methane with nitrogen dioxide in accordance with Equation 14.

Substituting the appropriate values of ΔH°_{298}, we obtain:

$$\Delta Z_{298}^\circ = 22.7 \text{ kcal.}$$

An analogous calculation for the reaction of propane with nitrogen dioxide gives the value ΔZ°_{298} = 20.1 kcal.

The temperature-dependence of the change of free energy in the reaction of methane with nitrogen dioxide in accordance with Equation 14 can be expressed, to a first approximation, by the formula:

$$\Delta Z_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298}.$$

Substituting the values

$$\Delta H^\circ_{298} = \Delta H^\circ_{298}CH_3 + \Delta H^\circ_{298}HNO_2 - \Delta H^\circ_{298}CH_4 - \Delta H^\circ_{298}NO_2$$

and

$$\Delta S^\circ_{298} = S^\circ_{298}CH_3 + S^\circ_{298}HNO_2 - S^\circ_{298}CH_4 - S^\circ_{298}NO_2$$

we arrive at the equation:

$$\Delta Z^\circ = 27 - 0.0012\ T. \quad (20)$$

From this equation it may be inferred that it is impossible to obtain methyl radicals by Reaction (14) at any temperature that could be used in practice in the vapor-phase nitration of alkanes.

Kireev [16] has shown that for reactions of the same type the difference between values of ΔH° (Equations 18 and 19) is independent of temperature, so that, on the basis of Equations 20 and 19 it may be inferred that the formation of free radicals by the general equation $RH(g) + NO_2(g) \rightarrow R(g) + HNO_2(g)$ (regarded from the macroscopic point of view) is very unlikely also for temperatures other than 25°.

The low potency of the monomeric form of nitrogen dioxide in the generation of radicals follows also from a comparison of values of ΔZ°_{298} for the typical reaction:

$$X + H_2 \rightarrow HX + H; \quad (21)$$

$$Cl + H_2 \rightleftarrows HCl + H; \quad Br + H_2 \rightleftarrows HBr + H; \quad I + H_2 \rightarrow HI + H;$$

$$\Delta Z^\circ_{298} = 0{,}6 \text{ kcal}; \quad \Delta Z^\circ_{298} = 16{,}5 \text{ kcal}; \quad \Delta Z^\circ_{298} = 34{,}3 \text{ kcal};$$

$$NO_2 + H_2 \rightarrow HNO_2 + H; \quad \Delta Z^\circ_{298} = 31{,}2 \text{ kcal}$$

These data show that the ability of NO_2 to break the H—H bond is approximately the same as that of atomic iodine. Actually, whereas a chain mechanism with participation of the above reactions has been established experimentally for chlorine and bromine, the reaction of iodine with hydrogen is not a chain reaction, but proceeds according to the equation:

$$H_2 + I_2 \rightleftarrows 2HI.$$

On the basis of thermochemical data Semenov [17] showed that NO_2 is again a radical of low activity in reactions of the type

$$R + R'X \rightarrow RX + R',$$

in which

$$R = NO_2,\ R' = CH_3,\ X = CH_3,\ NH_2.$$

As vapor-phase nitration, particularly with oxides of nitrogen, is carried out at temperatures below those required for the cracking of hydrocarbons, then, in view of the high energy required for the rupture of C—H bond (80-90 kcal/mole), it is very unlikely that free radicals will be generated thermally by the reaction:

$$RH \rightarrow R + H.$$

The thermodynamic calculations given above do not indicate the impossibility of the formation of radicals in the system RH (g) + NO_2 (g) in other ways.

The vapor-phase nitration of alkanes with nitrogen dioxide is usually carried out at 250-350° for a long (of the order of several minutes) period of contact. In view of the partial dissociation of nitrogen dioxide which undoubtedly occurs under these conditions, it may be possible to explain the primary radical formation on the basis of reaction of oxygen formed by dissociation of nitrogen dioxide with the alkane by the chain mechanism [18]:

$$RH + O_2 \rightarrow RO_2H.$$
$$RO_2H \rightarrow RO + OH.$$
$$OH + RH \rightarrow R + H_2O.$$
$$RO + RH \rightarrow ROH + R.$$
$$R + O_2 \rightarrow RO_2.$$
$$RO_2 + RH \rightarrow RO_2H + R \text{ etc.}$$

We must point out that, in some papers on the oxidation of hydrocarbons in presence of nitrogen dioxide [19, 20] and on the oxidation of hydrocarbons by pure nitrous oxide [21], it is assumed that reaction is initiated by oxygen atoms formed by the thermal dissociation of a nitrogen oxide. It is emphasized in the literature [5] that only the formation of alkyl radicals is a chain reaction, the combination of R and NO_2 being a free-radical reaction. As a result of the entry of the oxygen into reaction with the alkane, the dissociation equilibrium of NO_2 will be displaced with increase in the oxygen concentration, thus creating the conditions necessary for the formation of alkyl radicals. Alkyl radicals, by reacting with undecomposed NO_2 molecules, give nitroalkanes.

Data on the nitration of propane with nitrogen dioxide in the vapor phase at not above 300° in presence of oxygen show [5] that rise in oxygen concentration in the reaction zone, by increasing the opportunities for radical formation, raises the yield of nitroalkanes to an appreciable extent. When the same process is carried out at a higher temperature (350°), there is a sharp fall in the yield and extent of conversion and there is an appreciable increase in the CO content of the exit gases. It would appear that, in the high-temperature nitration of alkanes with nitrogen dioxide in presence of oxygen, conditions are created under which the rate of the reaction

$$R + NO_2 \rightarrow RNO_2$$

is evidently less than that of the reaction

$$R + O_2 \rightarrow \text{oxidation products.}$$

One of the possible causes of the development of an oxidative course in the nitration reaction lies in the thermal decomposition of nitrous esters, which, as Titov [7] showed, are formed as by-products in the nitration of alkanes with oxides of nitrogen. The study of the oxidation reactions of hydrocarbons shows that the addition of alkyl nitrites provides a means of introducing active initiating centers [22], which shorten the induction period and bring about a great increase in reaction rate [23].

According to Joffe [6], a mixture of pentane and nitrogen dioxide of composition $C_5H_{12} + 4NO_2$ reacts explosively at 432° under a pressure of 14.2 mm. The period of induction then observed (2.5 seconds) is reduced to zero when a trace of ethyl nitrite is added. In this paper [6] it is suggested that a critical concentration of nitrous esters may be formed during the induction period.

The initiation of radical formation in the vapor-phase nitration of alkanes with nitrogen oxides and nitric acid is closely related to other phenomena observed by various authors, namely, the catalysis of the reaction by chlorine [24, 25], bromine [26], iodine [26], and mixtures of these halogens with oxygen. According to a patent [27], when oxygen and halogens are used simultaneously, the degree of conversion of nitric acid is 50% greater than in the usual procedure, in which oxygen and halogens are not used.

The results of Maizus and Emanuel [28] on the catalytic effects of chlorine, bromine, and hydrogen halides (HCl and HBr) on the oxidation of hydrocarbons can be applied also to the nitration reaction, and they enable us to associate the observed accelerating effects of small additions of halogens with their initiation of radical formation, for example in accordance with the scheme [25]:

$$X_2 \rightleftharpoons 2X.$$
$$RH + X \rightarrow R + HX.$$
$$R + NO_2 \rightarrow RNO_2.$$
$$R + X_2 \rightarrow RX + X.$$
$$HX \xrightarrow{O_2,NO_2} H_2O + X_2.$$

In explanation of the primary generation of active halogen atoms, in particular chlorine atoms, Titov [7] proposed the following equations:

$$Cl_2 + NO \rightarrow NOCl + Cl.$$
$$Cl_2 + NO_2 \rightarrow NO_2Cl + Cl.$$

In vapor-phase nitration of alkanes with nitrogen dioxide, increase in the yield of nitroalkane can be attained both by increase in the rate of radical formation and by retardation of oxidative reactions in which the free radicals take part. It is probable that the catalytic effect of molecular iodine on the nitration of propane with nitrogen dioxide observed by Bachman and others [26] is to be associated largely with the tendency of rather inactive iodine atoms to retard the oxidation of hydrocarbons in particular cases. Actually, it is found that in presence of 0.15% I_2 [26] the CO content of the reaction products is reduced from 22.1% to 5.2% [26]. Simultaneously, the yield of nitro compounds is increased by 10%.

The presence of free nitric oxide in the sphere of reaction has an unfavorable effect on the nitration reaction. Nitric oxide may be formed both by the dissociation of nitrogen dioxide and also by the reaction:

$$2RH + 3NO_2 \rightarrow 2RNO_2 + NO + H_2O.$$

The effect of nitric oxide is particularly notable in the nitration of propane with nitric acid at 420° [25]. At a molar ratio of $NO/HNO_3 = 0.009$, in spite of the presence of oxygen ($O_2/HNO_3 = 1.05$), the degree of conversion of HNO_3 was reduced from 38.9% (NO absent) to 34.5% (NO present). At the same time the CO content of the exit gases rose from 6.2% to 11.9%, and the ethylene content rose from 2.3% to 5.7%.

Being a powerful inhibitor of chain reactions [29], nitric oxide reduces the rate of radical formation and the rate of combination of radicals with nitrogen dioxide. On the other hand, the increases observed in the CO and C_2H_4 contents of the exit gases indicates the development of processes of hydrocarbon cracking and of far-reaching oxidation of hydrocarbons.

In the papers of Shtern and coworkers [30, 31] on the oxidation of propane by oxygen in presence of nitrogen dioxide, the shortening of the induction period is considered to be due to the effect of nitric oxide formed by dissociation. However, the addition of nitric oxide inhibits the oxidation of propane by nitrous oxide in the temperature range 505-605° [32]. Above 655° the inhibiting effect of nitric oxide disappears. As Semenov has pointed out [17], nitric oxide can simultaneously show both accelerating and retarding effects on chain reactions; the overall effect may be positive or negative.

SUMMARY

It is shown with the aid of thermodynamic calculations that it is very unlikely that free radicals will be formed by reaction of nitrogen dioxide with alkanes in accordance with the equation $RH + NO_2 \rightarrow R + HNO_2$.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 17. PARTICIPATION OF 2-BUTENE IN THE HYDROCONDENSATION REACTION WITH CARBON MONOXIDE

Ya. T. Eidus and R. I. Izmailov

We have previously reported results on the hydrocondensation of carbon monoxide with 1-butene [1] and 2-butene [2] under identical conditions: temperature 190°, pressure atmospheric, carbon monoxide concentration 4-6% on the original gas mixture of 70-75% butene and 20-25% hydrogen, space velocity about 100 hour^{-1}. Comparison of the hydrocondensation products of 1-butene and 2-butene*, of the physical constants of fractions having an identical boiling range, and of the Raman spectra of these fractions shows that these products do not differ qualitatively and consist essentially of hydrocarbons of normal structure: there is an admixture of only a very small amount of branched hydrocarbons having one methyl side group. This result was very unexpected for reaction with 2-butene, since normal hydrocarbons can be formed by hydrocondensation only from 1-butene: as in this process the reaction center in the olefin molecule is the double bond, 2-butene should give only branched hydrocarbons. The mild conditions of the reaction practically exclude the possibility of skeletal isomerization. Hence, if unchanged 2-butene were to undergo the hydrocondensation reaction at any appreciable rate, it would be expected that appreciable amounts of branched hydrocarbons would be found among the reaction products, which is not observed experimentally. The same could be said of the products of the hydrocondensation of 1-butene, for it has been shown previously [3] that 1-butene is readily isomerized to 2-butene under the conditions of the reaction.

Our results give reason to suppose that, in the hydrocondensation of 1- or 2-butene, the products are always formed from 1-butene, into which 2-butene must first be isomerized. On this basis we should expect that no difference would be observed between 1- and 2-butenes in the hydrocondensation reaction. However, when the results on the hydrocondensation of carbon monoxide with 1-butene [1] and with 2-butene [2] are compared, not only resemblances, but also substantial differences can be observed.

The identical extents to which hydrogen participates in the overall process should be noted: in both cases it reacts to the extent of 54-55%, calculated on the original amount of hydrogen. There is little difference also in the extents to which carbon monoxide takes part: 52.2% in the case of 1-butene and 45.6% in the case of 2-butene. The same may be said of the hydrocracking products, which amount to not more than 3-4% of the 1- or 2-butene that undergoes reaction. Among the differences that should be noted we must first of all refer to the considerable difference in the value of the total yield of liquid hydrocarbons: 730-975 ml/cu.m, or 70-100 ml/liter·hour, for the reaction of 1-butene and 350-540 ml/cu.m, or 35-55 ml/liter·hour, for the reaction of 2-butene (ratio about 2). Correspondingly, the degree of conversion of 1-butene is 74%, and that of 2-butene is 47%. There is a difference also in the content of unsaturated hydrocarbons in the hydrocondensate (52% and 37%); moreover, the average molecular weight of these is greater in the case of 2-butene, as can be seen from the relative amounts of heavy and light oils and the sizes of the individual fractions. In the hydrogenated hydrocondensate the C_8 fractions amount to 8% and 0.8% respectively, the C_8 fractions to 8.6% and 6.1%, and the C_7 fractions to 9.7% and 8.4%. The yield of butane, which characterizes the hydrogenation of the butenes, is 9.4% for 1-butene and 5.0% for 2-butene (on the amount of original olefin that reacted). This increased yield of butane and greater total yield of hydrocarbons in the reaction with 1-butene must explain the equal extent to which hydrogen takes part in the two cases.

At first glance it may appear that all those features of the 2-butene reaction which we have described as

* See Table 3 and Fig. 2 in our Communications 15 [1] and 16 [2].

substantially different from those of the 1-butene reaction must contradict the view that the hydrocondensation products from 2-butene are formed essentially from 1-butene, into which 2-butene is first isomerized. However, on a closer examination it is found that these differences not only do not contradict this view, but, on the contrary, find their explanation in this general scheme of reaction and confirm the hypothesis that the rate of the reaction of 1-butene in hydrocondensation with carbon monoxide is very much greater than the rate for 2-butene, the direct reaction of which is extremely slow:

$$^{v}C_4H_8\text{-}1 \gg {}^{v}C_4H_8\text{-}2; \quad {}^{v}C_4H_8\text{-}2 \to 0, \tag{1}$$

and that the hydrocondensation reaction of 2-butene proceeds essentially via the intermediate formation of 1-butene.

Let us examine the relative amounts of the reactants on the catalyst surface in the two cases. In the reaction with 1-butene, the catalyst contains adsorbed hydrogen, carbon monoxide, 1-butene, and a fairly large amount of 2-butene, which is formed from 1-butene and will not exceed the latter in amount. We have shown previously [3] that, under the same reaction conditions but in absence of carbon monoxide, the relative amounts of 1- and 2-butenes in the gas phase of the reaction product is 1 : 1.1 when the original hydrocarbon is 1-butene (in presence of hydrogen). It was found also [1] that, when carbon monoxide is added, the amount of 1-butene that isomerizes to 2-butene is 16% on the amount of olefin that reacts. Hence, for the butene concentrations at the catalyst surface in experiments on the hydrocondensation of carbon monoxide with 1-butene we may write:

$$[C_4H_8 - 1]' \geq [C_4H_8 - 2]'. \tag{2}$$

When the original hydrocarbon is 2-butene, hydrogen and carbon monoxide are adsorbed on the catalyst surface in about the same amounts as in the experiments with 1-butene; 2-butene and small amounts of 1-butene formed from 2-butene are also adsorbed. The fact that the 1-butene concentration is indeed low in this case is clear from the results of our previous investigations [1, 3], in which no 1-butene could be detected in the gas phase after experiments with mixtures of 2-butene, hydrogen, and carbon monoxide or of 2-butene and hydrogen. The explanation is that, when the volume of the original 2-butene is comparatively small, the 1-butene formed from it in small amount remains adsorbed on the catalyst surface; in presence of carbon monoxide it enters the hydrocondensation reaction, being continually regenerated by isomerization from 2-butene.

Hence, for the butene concentrations at the catalyst surface in experiments on the hydrocondensation of carbon monoxide with 2-butene we may write:

$$[C_4H_8 - 2]' \gg [C_4H_8 - 1]'. \tag{3}$$

However, it is clear from experiments on the isomerization of 1- and 2-butenes [3] that

$$[C_4H_8 - 2]' \geq [C_4H_8 - 2] \tag{4}$$

and from (3) and (4) it follows that

$$[C_4H_8 - 2]' \gg [C_4H_8 - 1]', \tag{5}$$

and from (2) and (5) we have

$$[C_4H_8 - 1]' \gg [C_4H_8 - 1]'. \tag{6}$$

On the basis of the above considerations it follows that

$$\frac{[H]'}{[C_4H_8 - 1]'} \gg \frac{[H]}{[C_4H_8 - 1]} \tag{7}$$

and

$$\frac{[CO]'}{[C_4H_8 - 1]'} \gg \frac{[CO]}{[C_4H_8 - 1]}, \tag{8}$$

in which [H]' and [CO]' are the hydrogen and carbon monoxide concentrations (expressed in any form) at the catalyst surface in experiments with 1-butene and [H]" and [CO]" are the corresponding concentrations for experiments with 2-butene.

The relationship (7) shows that, in the hydrocondensation of carbon monoxide with 2-butene, the ratio of the hydrogen concentration to the concentration of 1-butene reacting is greater than the same ratio for reaction with 1-butene. As shown previously [1], a relative increase in the hydrogen concentration results mainly in a fall in the total yield of liquid hydrocarbons, an increase in their saturation, and, finally, a lowering of their average molecular weight. In the hydrocondensation of carbon monoxide with 2-butene the total yield of hydrocarbons is indeed lower and the reaction product is more saturated than in the 1-butene reaction. The average molecular weight, however, is not lower, but higher. This unexpected contradiction is completely resolved by an examination of the relationship (8), from which it can be seen that in the hydrocondensation of carbon monoxide with 2-butene the ratio of the concentrations of carbon monoxide and 2-butene at the catalyst is very much greater than for the same reaction with 1-butene. As we have already found [4], a relative increase in the carbon monoxide concentration results in an increased yield of the heavier hydrocarbons; moreover, increase in the carbon monoxide concentration beyond a definite limit results in retardation of the reaction and fall in overall yield. Hence, increases in the concentrations of hydrogen and of carbon monoxide have antagonistic effects on the average molecular weight of the reaction products. It would appear that in this case the effect of carbon monoxide is predominant, so that in experiments with 2-butene the product is heavier than in the 1-butene reaction.

We must consider yet another peculiarity observed in the hydrocondensation of carbon monoxide with 1-butene: the presence of isopentene in the hydrocondensate, which was not found in the 2-butene reaction. In the latter reaction the total yield of the C_5 fraction was only 0.8% of the liquid hydrocondensate [2], which is probably to be explained by the effect of the enhanced carbon monoxide concentration at the catalyst surface and the more rapid further hydrocondensation of the pentenes formed.

It is very probable that the branched pentene isomers are formed mainly not from 2-butene, but from 1-butene by the mechanism indicated previously [2]. In fact, if they arise from 2-butene, then the inequalities (4) and (6) indicate that we must expect the greater amounts of branched C_5 hydrocarbons not in the 1-butene experiments, but in hydrocondensation of carbon monoxide with 2-butene, which is not observed experimentally.

SUMMARY

1. The products of the hydrocondensation of carbon monoxide with 1-butene and with 2-butene are in both cases mainly normal aliphatic hydrocarbons admixed with a very small amount of slightly branched hydrocarbons.

2. In the hydrocondensation of carbon monoxide with 1-butene, a more unsaturated, lighter product is obtained than in the same reaction with 2-butene.

3. A comparison of our results on the two reactions enables us to infer that the mechanism is the same in both cases, but in the 2-butene reaction the 2-butene is largely isomerized into 1-butene, which then undergoes hydrocondensation with carbon monoxide.

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MECHANISM OF THE THERMAL DECOMPOSITION AND CHLORINOLYSIS OF HEXACHLOROPROPENE AND OCTACHLORO-1,3-PENTADIENE

M. G. Gonikberg

This paper gives an analysis of available data on the pyrolysis of hexachloropropene and octachloro-1,3-pentadiene at 450-500° in a flow system at atmospheric pressure, and also on the chlorinolysis of these compounds [1], our object being the elucidation of various aspects of the mechanism of these reactions.

Among compounds formed in the thermal decomposition of hexachloropropene are carbon tetrachloride, tetrachloroethylene, hexachloroethane, the compound C_6Cl_8 (see below), and hexachlorobenzene. The first stage of the process may consist either in the elimination of a chlorine atom (Reaction Ia, Ib, and Ic), in the breaking of a C—C bond (Reaction Id), or in disproportionation of chlorine (Reaction IIa):

$$CCl_2=CCl-CCl_3 \rightarrow CCl_2=\dot{C}Cl-\dot{C}Cl_2 + \dot{C}l. \quad (Ia)$$

$$CCl_2=CCl-CCl_3 \rightarrow CCl_2=\dot{C}(CCl_3) + \dot{C}l. \quad (Ib)$$

$$CCl_2=CCl-CCl_3 \rightarrow \dot{C}Cl=CCl-CCl_3 + \dot{C}l. \quad (Ic)$$

$$CCl_2=CCl-CCl_3 \rightarrow CCl_2=\dot{C}Cl + \dot{C}Cl_3. \quad (Id)$$

$$2C_5Cl_6 \rightarrow C_5Cl_5 + C_5Cl_7. \quad (IIa)$$

The rates of reactions of Types I and II are determined by the equations [2]:

$$\omega_I \approx 10^{13} e^{-E_I/RT} c \quad (1)$$

and

$$\omega_{II} \approx 10^{-10} e^{-E_{II}/RT} c^2, \quad (2)$$

in which c is the number of molecules per cc; at 500° and 1 atm, $c \approx 10^{19}$.

$$\frac{\omega_I}{\omega_{II}} \approx 10^{4} e^{-(E_I - E_{II})/RT}. \quad (3)$$

We shall now examine some data on the C—Cl and C—H bond energies in aliphatic compounds (Table 1).

For the compounds given in Table 1:

$$Q_{C-Cl} \approx Q_{C-H} - 19(\pm 1.5) \text{ kcal/mole}.$$

From Table 1 we conclude $E_{(Ia)} \approx 40$-50 kcal/mole and $E_{(Ic)} \approx 60$-80 kcal/mole. In order to evaluate $E_{(Ib)}$ we may use the data for Q_{C-H} in $(CH_3)_3CH$—H (89 kcal/mole). When we take into account the replacement of an ordinary bond by a double one and hydrogen atoms by chlorine, we find that $E_{(Ib)}$ must also be more than 60 kcal/mole. The same may be inferred for $E_{(Id)}$ on the basis of data for Q_{C-C} in CH_2=CH—CH_3 (90 kcal/mole?) and in CH_3CH_2—CH_3 (82 kcal/mole). Hence, on the basis of these very approximate estimates we may state, with a high measure of confidence, that, of the possible reactions of unimolecular decomposition of hexachloropropene, Reaction (Ia) has the lowest activation energy.

TABLE 1

Some C—Cl and C—H Bond Energies [2]

Compound	Q_{C-Cl} (kcal/mole)	Compound	Q_{C-H} (kcal/mole)	$Q_{C-H}-Q_{C-Cl}$
CCl_3-Cl	68.4	CCl_3-H	89	20.6
$CHCl_2-Cl$	73.5	$CHCl_2-H$	93.2	19.7
CH_2Cl-Cl	78.5	CH_2Cl-H	97.4	18.9
CH_3-Cl	83.5	CH_3-H	101	17.5
CH_3CH_2-Cl	80	CH_3CH_2-H	98	18
$CH_2=CH-Cl$	86?	$CH_2=CH-H$	104?	18?
$CH_3CH_2CH_2-Cl$	77	$CH_3CH_2CH_2-H$	95	18
$CH_2=CHCH_2-Cl$	58	$CH_2=CHCH_2-H$	77	19

There is very little information in the literature on the activation energies of reactions of Type II. The following values of E are known for reactions in which two radicals are formed by reaction between two molecules (with participation of olefins [2]): $C_2H_4 + C_2H_6 \rightarrow 2\dot{C}_2H_5$ ($E \approx 60$ kcal/mole); $Cl_2 + C_2H_4 \rightarrow \dot{C}_2H_4Cl + \dot{C}l$ ($E \approx 41$ kcal/mole); in the polymerization of olefins E = 35-38 kcal/mole. Let us assume a minimal activation energy (35-40 kcal/mole) for Reaction (IIa). Then it follows from Equation 3 ($E_{(Ia)} = 50$ kcal/mole and $E_{(IIa)} = 35$ kcal/mole) that

$$\omega_{(Ia)} \gg \omega_{(IIa)}.$$

If however we take account of the fact that there are undoubtedly steric difficulties in Reaction (IIa) (steric factor $f < 1$), we obtain

$$\omega_{(Ia)} > \omega_{(IIa)}. \qquad (4)$$

In our opinion, therefore, the most probable first stage in the thermal decomposition of hexachloropropene is Reaction (Ia), which proceeds with formation of the radical $\dot{C}_3Cl_5$. The compound C_6H_{10} is not found among the reaction products, but the presence of C_6Cl_8 (see below) has been established. This suggests that in the course of reaction either a diradical $\dot{C}_3Cl_4\dot{C}$ is formed, or a molecule of the same composition (tetrachloroallene or chloro(trichloromethyl)acetylene).

Let us now examine the reaction between the atomic chlorine formed by Reaction (Ia) with the original hexachloropropene. We consider that this reaction is a process of destructive chlorination, which, unlike the usual chlorinolysis, proceeds in absence of excess of chlorine. In our opinion, the mechanism of destructive chlorination is to some extent analogous to that of the homogeneous destructive hydrogenation of aromatic compounds [3, 4]: it is a peculiar radical reaction of substitution distinguished by the fact that the interaction of the atom (radical) with the molecule results in the removal from the molecule not of an atom, but of a more or less complex radical. In the case of a molecule containing a double bond, this interaction appears to occur in two stages: addition of the attacking atom (radical) at the double bond, and breakdown of the resulting radical at the C—C bond [5].

Thus, the following scheme is possible for hexachloropropene:

$$\dot{C}_3Cl_4 + \dot{C}l \rightarrow \dot{C}_3Cl_5;$$
$$\dot{C}_3Cl_5 \rightarrow C_2Cl_4 + \dot{C}Cl_3.$$

It will be shown below that the hypothesis that we have advanced for the main stages of the thermal decomposition of hexachloropropene is confirmed by the compositions and relative amounts of the reaction products. Owing to the absence of accurate kinetic data we cannot completely exclude the possibility of a chain mechanism for the reaction under consideration; below, however, we shall give our proposed radical non-chain scheme, which, in our opinion, is in fairly satisfactory agreement with experiment.

Let us pass to an examination of experimental results obtained in a flow system for a time of contact of 12-15 seconds. Results on the investigation of the pyrolysis of hexachloropropene are given in Table 2.

TABLE 2

Main Products of the Vapor-phase Pyrolysis of Hexachloropropene (yields in moles/mole of original C_3Cl_6)[1]

Temperature (°C)	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6
450-460	0.04	0.28	0.12	0.57
490-500	0.11	0.67	0.21	Traces
490-500	0.14	0.70	0.24	Traces
Mean for 490-500	0.125	0.685	0.225	

The authors of the paper cited [1] state that in the high-boiling fractions they identified considerable amounts of the crystalline compound C_6H_8 (which they considered to be 1,2,3,4,5-pentachloro-5-(trichloromethyl)-1,3--cyclopentadiene) and hexachlorobenzene. It was shown by special experiments that the hexachlorobenzene was formed by the thermal decomposition of C_6Cl_8*.

With the aid of Table 2 we may calculate the material balance sheet and determine the composition of the high-boiling residue. It is found that at 450-460° the composition of the residue corresponds to the formula $C_nCl_{1.29n}$, and at 490-500°, $C_nCl_{1.33n}$. Assuming that n = 6, we find that at 450-460° the formula of the residue is $C_6Cl_{7.74}$, and at 490-500°, C_6Cl_8. The yields (calculated for C_6Cl_8) are, respectively, 0.075 and 0.168 moles per mole of original C_3Cl_6.

Hexachloro-1,2-butadiene was not detected among the reaction products. This indicates that $\dot{C}_2Cl_3$ radicals are not formed in the thermal decomposition of hexachloropropene and that there is therefore an absence of C—C bond rupture in accordance with the equation:

$$Cl_3C{-}CCl{=}CCl_2 \longrightarrow Cl_3\dot{C} + \dot{C}_2Cl_3.$$

We therefore propose the following scheme for the mechanism of the reaction:

$$1.\ a\,C_3Cl_6 \rightarrow a\,C_3Cl_4 + 2a\,\dot{C}l.$$

$$2.\ a\,C_3Cl_4 \rightarrow \frac{a}{2}\,C_6Cl_8.$$

$$3.\ b\,C_3Cl_6 + b\,\dot{C}l \rightarrow b\,C_2Cl_4 + b\,\dot{C}Cl_3.$$

$$4.\ (2a-b)\,\dot{C}l + (2a-b)\,\dot{C}Cl_3 \rightarrow (2a-b)\,CCl_4.$$

$$5.\ (2b-2a)\,\dot{C}Cl_3 \rightarrow (b-a)\,C_2Cl_6.$$

$$(a+b)\,C_3Cl_6 \rightarrow \frac{a}{2}\,C_6Cl_8 + b\,C_2Cl_4 + (b-a)\,C_2Cl_6 + (2a-b)\,CCl_4$$

It follows from the overall equation for the process that the number of moles of hexachloropropene entering into reaction [we shall denote this by (C_3Cl_6)] equals the sum of the number of moles of tetrachloroethylene and the number of moles of C_6Cl_8, i. e., $(C_3Cl_6) = (C_2Cl_4) + 2(C_6Cl_8)$; also $(C_2Cl_6) = (C_2Cl_4) - 2(C_6Cl_8)$ and $(CCl_4) = 2(C_6Cl_8) - (C_2Cl_6)$.

Actually, these relationships hold very satisfactorily at 450-460°: 0.43 should equal 0.28 + 0.15; 0.12 should equal 0.28 − 0.15; 0.04 should equal 0.15 − 0.12. At 490-500°, however, there is a great departure from the second of these relationships (in the calculation we used average values from two experiments; see Table 2), and this makes it necessary to supplement the above mechanism scheme by the reaction between $\dot{C}Cl_3$ radicals and C_3Cl_6 molecules:

$$\dot{C}Cl_3 + C_3Cl_6 \rightarrow C_2Cl_4 + \dot{C}_2Cl_5;$$
$$2\dot{C}_2Cl_5 \rightarrow C_2Cl_4 + C_2Cl_6.$$

* These authors showed also that, under the conditions used, the chlorination of C_2Cl_4 to C_2Cl_6 did not occur to any appreciable extent, even at 400-500°.

To Equations 1-4 we must now add the following:

$$5a.\ c\,\dot{C}Cl_3 \rightarrow \frac{c}{2}\,C_2Cl_6.$$

$$6.\ (2b-2a-c)\,\dot{C}Cl_3 + (2b-2a-c)\,C_3Cl_8 \rightarrow$$

$$\rightarrow \left(3b-3a-\frac{3}{2}c\right)C_2Cl_4 + \left(b-a-\frac{c}{2}\right)C_2Cl_6.$$

$$(3b-a-c)\,C_3Cl_8 \rightarrow \frac{a}{2}\,C_6Cl_6 + \left(4b-3a-\frac{3}{2}c\right)C_2Cl_4 +$$
$$+ (b-a)\,C_2Cl_6 + (2a-b)\,CCl_4$$

Two relationships follow from the overall equation of the process:

a) (CCl_4) should equal $2(C_6Cl_6) - (C_2Cl_6)$;
b) $3(C_3Cl_8)$ should equal $2(C_2Cl_4) + (C_2Cl_6) + 8(C_6Cl_6)$.

It is easy to show that both of these relationships are true both at 450-460° and at 490-500°, which is a powerful argument in favor of the proposed mechanism scheme.

The same scheme enables us to explain also the results of experiments [1] on the chlorinolysis of hexachloropropene (Table 3).

TABLE 3
Products of the Chlorinolysis of Hexachloropropene (yields in moles/mole original C_3Cl_6)

Temperature (°C)	CCl_4	C_2Cl_4	C_2Cl_6	C_3Cl_6
300-310	0.08	0.09	0	0.88
350-360	0.62	0.69	0.02	0.26
400-410	0.92	0.96	0.04	0
490-500	0.90	0.90	0.12	0

TABLE 4
Products of the Pyrolysis of Octachloropentadiene in the Vapor Phase (moles/mole original C_5Cl_8)

Temperature (°C)	CCl_4	C_4Cl_6	C_5Cl_6	C_6Cl_6	C_5Cl_8
400-410	0.01	0.03	0.04	0	0.8
450-460	0.22	0.36	0.30	0.02	0.25
490-500	0.37	0.42	0.39	0.08	0

It is evident that the chlorinolysis of hexachloropropene proceeds by the chain reaction scheme:

1) $C_3Cl_6 + \dot{C}l \rightarrow C_2Cl_4 + \dot{C}Cl_3$;
2) $\dot{C}Cl_3 + Cl_2 \rightarrow CCl_4 + \dot{C}l$;
3) $\dot{C}Cl_3 + \dot{C}l \rightarrow CCl_4$ } chain termination
4) $2\dot{C}Cl_3 \rightarrow C_2Cl_6$ }

To a slight extent, there occurs also addition of chlorine to C_2Cl_4 according to the scheme:

5) $C_2Cl_4 + \dot{C}l \rightarrow \dot{C}_2Cl_5$.
6) $2\dot{C}_2Cl_5 \rightarrow C_2Cl_6 + C_2Cl_4$.

The occurrence of these two last reactions results in a reduction in the yield of C_2Cl_4 and an increase in the yield of C_2Cl_6 at 490-500° (Table 3).

Let us pass to an examination of data on the pyrolysis of octachloro-1,3-pentadiene (Table 4) [1].

On the basis of the above considerations, the mechanism of the process may be represented as follows:

$$1.\ a C_5Cl_8 \rightarrow a C_5Cl_6 + 2a \dot{C}l.$$

$$2.\ b C_5Cl_8 + b \dot{C}l \rightarrow b \dot{C}Cl_3 + b C_4Cl_6.$$

$$3.\ (2a - b) \dot{C}Cl_3 + (2a - b) \dot{C}l \rightarrow (2a - b) CCl_4.$$

$$4.\ (2b - 2a) \dot{C}Cl_3 \rightarrow (b - a) C_2Cl_6.$$

$$(a + b) C_5Cl_8 \rightarrow a C_5Cl_6 + b C_4Cl_6 + (2a - b) CCl_4 + (b - a) C_2Cl_6$$

It was actually found that the yield of CCl_4 at 450-500° was approximately equal to $2(C_5Cl_6) - (C_4Cl_6)$. The authors of this paper do not give the yield of C_2Cl_6, but it follows from the overall equation that this yield must be very low (only 0.03 mole per mole of original C_5Cl_8 at 490-500°).

TABLE 5

Products of the Chlorinolysis of Octachloro-1,3-pentadiene (moles per mole of original C_5Cl_8)

Temperature (°C)	CCl_4	C_4Cl_6	C_5Cl_6	C_5Cl_8
350-360	0.13	0.14	0.05	0.79
400-410	0.56	0.59	0.20	0.16
490-500	0.60	0.62	0.27	0.004

Data on the chlorinolysis of C_5Cl_8 (Table 5) [1] are in full accord with the above scheme. As can be seen from the data in Table 5, the yield of C_4Cl_6 is only slightly higher than that of CCl_4, i. e., almost all of the $\dot{C}Cl_2$ formed reacts with chlorine. The chain process develops in accordance with the scheme:

$$1.\ Cl_2C{=}CCl{-}CCl{=}CCl{-}\dot{C}Cl_2 + \dot{C}l \rightarrow CCl_2{=}CCl{-}CCl{=}{=}CCl_2 + \dot{C}Cl_2,$$

$$2.\ \dot{C}Cl_3 + Cl_2 \rightarrow CCl_4 + \dot{C}l.$$

It may be assumed that the scheme of destructive chlorination (chlorinolysis) proposed in this paper is fairly general in character.

SUMMARY

1. On the basis of data on the thermal decomposition of hexachloropropene and octachloro-1,3-pentadiene, some conclusions are drawn about the mechanism of these processes.

2. A mechanism scheme is proposed for the destructive chlorination of halogen-substituted unsaturated hydrocarbons containing a carbon-carbon single bond. The basis of the scheme is the concept of the addition of a chlorine atom at the double bond and subsequent breakdown of the resulting radical at the C—C bond.

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* T.p. = C. B. Translation pagination.

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CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR

A general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR was held on April 25 and 26, 1956, under the chairmanship of Academicians I. I. Chernyaev and V. A. Kargin.

Academician V. A. Kargin read a paper entitled "Multichamber High Tension Electrodialysis". It is well known, said the speaker, that ordinary electrodialysis is a process for the purification of colloidal systems from electrolytes in which the latter are allowed to diffuse through semipermeable membranes, the rate of diffusion being increased by the application of an electric field. This process is often complicated by the presence of membrane potentials, which hinder the passage of some of the ions. These difficulties can be removed either by suitable choice of membrane or by the application of sufficiently high potential differences. New possibilities arise from the use of membranes prepared from ion-exchange resins, which permit the passage only of ions of one sign. Academician Kargin pointed out that, apart from the removal of electrolytes, the reverse process of diffusion of extracted substances into the substance being purified always occurs. When the rates of these processes become equal, an equilibrium is established and purification does not proceed further. Further purification or extraction of electrolytes requires the removal of the substances already extracted, which is usually achieved by changing the water in the side chambers of the electrodialyzer, in which the electrolytes are collected. This procedure complicates, and sometimes excludes, the use of electrodialysis for analytical purposes, and for the purification of substances very large amounts of very pure water are required. Instead of changing the water in the side chambers, we may cause it to circulate continuously through ion-exchange resins. Electrolytes are extracted in the form of the corresponding acids and bases, which are readily absorbed by the resins. This makes it possible to use no extra water at all and to speed up purification to such an extent that it is effective even for weak electrolytes. An example of this procedure is the purification of gelatin with isolation of the structure-forming part of the gelatin. A second method of extraction and concentration depends on the addition of two extra chambers of small volume connected to the side chambers by narrow channels. By the application of a further difference in potential the extracted electrolytes can be collected in a small volume of liquid for analytical purposes, or the purification can be carried out very rapidly and almost without consumption of water.

Apart from the purification of insoluble substances from electrolytes, the insoluble substances may be separated from one another by carrying out chemical reactions in the electrodialyzer itself which will selectively bring one or other substance into solution in the form of an electrolyte. The rates of such reactions in precipitates are dependent on the rates of diffusion determining the supply of the substances to be introduced and the removal of the substances formed. When these reactions are carried out in an electric field, the rates at which the ions move are correspondingly increased. Reacting electrolytes are introduced into the side chambers in such a way that the reacting ions pass through the mass of the substance to be purified. V. A. Kargin has called this method "purification in a stream of ions".

The high rates of purification in high tension electrodialysis make it possible to purify not only insoluble substances, but also solutions, and the use of a five-chamber electrodialyzer having thick membranes enables purification to be effected with small losses of the substance being purified. It is possible also to separate several solutes by the use of electrodialyzers having 10-20 chambers. In this case, under stationary conditions a definite pH is established in each chamber, and, on introduction of a mixture of salts, the metals are separated as oxides, which are precipitated in different chambers. Multichamber electrodialysis can be used also for the synthesis of substances formed from extremely dilute solutions. Several minerals were synthesized in this way, and crystalline

aluminosilicates were prepared by direct reaction between silicic acid and alumina in aqueous solutions at ordinary temperatures.

In illustration of his address, Academician Kargin gave demonstrations of various kinds of apparatus used by him in the laboratory. Corr. Member Acad. Sci. USSR B. V. Nekrasov, K. V. Chibisov, Doctor Chem. Sci., K. T. Poroshin, and R. P. Lastovsky, in discussing the paper, remarked on the great interest of the method and its high practical importance. In some of the works manufacturing chemical reagents high tension electrodialyzers were already in use for the removal of traces of impurities in the course of the preparation of chemically pure substances. The greatest obstacle to the extensive introduction of this method into practice is the lack of apparatus, which is not yet being manufactured.

Doctor of Chemical Sciences O. E. Zvyagintsev, (co-author E. F. Karandasheva) read a paper entitled "Rate of the Replacement of Ligands in Quadrivalent Platinum Complex Compounds as a Measure of the Trans Effect".

The trans effect, stated O. E. Zvyagintsev, is manifested in complex compounds in which the complex has a square or octahedral structure by the fact that the rate at which a ligand attached to the central atom is replaced is determined by the nature of the ligand occupying the trans position. An investigation into the kinetics of replacement in platinum compounds was undertaken with the object of characterizing the trans effect quantitatively.

The kinetics of replacement were studied for some reactions of bivalent platinum compounds, including:

$$K(PtNH_3Cl_3) + Py^* \rightarrow (PtNH_3ClPyCl) + KCl; \quad (1)$$
reaction coordinate Cl—Pt—Cl

$$K(PtNH_3ClBr) + Py \rightarrow (PtNH_3ClPyBr) + KCl; \quad (2)$$
reaction coordinate Br—Pt—Cl

$$K(PtNH_3ClNO_2Cl) + Py \rightarrow (PtNH_3ClPyNO_2) + KCl; \quad (3)$$
reaction coordinate NO_2—Pt—Cl

$$K[Pt(C_2H_4)Cl_3] + Py \rightarrow [Pt(C_2H_4)PyCl_2] + KCl; \quad (4)$$
reaction coordinate C_2H_4—Pt—Cl.

It was shown that the most reactive coordinate in platinous compounds is the coordinate (2). Replacement reactions on this coordinate are characterized by the highest rate constant and the lowest activation energy.

If the trans activity of a ligand is measured by the value of the rate constant, then the trans activity of a nitro group is ten times as high as that of chlorine, and the trans activity of bromine is three times as high as that of chlorine.

The kinetics of replacement in quadrivalent platinum compounds were investigated for the reactions:

$$[(NH_3)_3PtCl_3]Cl + Py \rightarrow [(NH_3)_3ClPtPyCl]Cl_2; \quad (5)$$
reaction coordinate Cl—Pt—Cl

$$[(NH_3)_3PtClBrCl]Cl + Py \rightarrow [(NH_3)_3ClPtPyBr]Cl_2; \quad (6)$$
reaction coordinate Br—Pt—Cl

$$[(NH_3)_3PtClNO_2Cl]Cl + Py \rightarrow [(NH_3)_3ClPtPyNO_2]Cl_2; \quad (7)$$
reaction coordinate NO_2—Pt—Cl

and also some other reactions, selected so as to permit investigations into the effect of a nitro group in the cis position relative to a chlorine that was undergoing replacement, the effect of the presence of a cyclic ethylenediamine group, and other factors.

The kinetic studies showed that replacement reactions are somewhat slower for the quadrivalent platinum compounds.

In quadrivalent platinum compounds the coordinate (7) is the least reactive, for it has the lowest rate constant and the highest activation energy.

The experiments on three of these compounds were repeated in acetone. It was found that the rates of re-

* Py = pyridine.

placement were almost identical in water and in acetone. A comparison of the rate constants for bi- and quadrivalent platinum compounds showed that the values for quadrivalent platinum are considerably lower than those for bivalent platinum compounds having the same reaction coordinates. The trans effect of bromine, as measured by the rate constant for the replacement of the opposite ligand, was found to be three times as great as that of chlorine both in bivalent and in quadrivalent platinum compounds. The nitro group behaves essentially differently in bivalent and in quadrivalent platinum compounds: its trans effect in compounds of bivalent platinum is very much greater than in compounds of quadrivalent platinum; in the latter it is considerably lower than that of chlorine and bromine.

As the speaker pointed out, the study of the kinetics of ligand replacement permits an estimation of the cis effects of various ligands, including cyclic ligands. The cis effect is very small in comparison with the trans effect.

From the results cited, said O. E. Zvyagintsev, we may conclude that the study of the kinetics of replacement in complex compounds of bi- and quadri-valent platinum makes it possible to make quantitative estimates of the trans activities of ligands.

Corr. Member Acad. Sci. USSR B. V. Nekrasov, Ya. K. Syrkin, and Doctor Chem. Sci. M. M. Yakshin, and others took part in the discussion on this paper and pointed out the importance of the investigation.

B. A. Dolgoplosk, Doctor Chem. Sci., read a paper entitled "Initiation of Free Radical Reactions in Aqueous and Hydrocarbon Media". He pointed out that the decomposition of many organic compounds into free radicals in hydrocarbon solutions usually proceeds at bonds between oxygen and oxygen, nitrogen and nitrogen, nitrogen and sulfur, carbon and nitrogen, sulfur and sulfur, etc. This process occurs particularly readily when such bonds are conjugated with an unsaturated bond or with an aromatic nucleus. Azo compounds, unlike peroxide, triazenes, hydroperoxides, and other substances, decompose in accordance with a unimolecular law, irrespective of their concentration in solution or the presence of reducing agents in the system. Aliphatic-aromatic triazenes are convenient sources of free radicals in hydrocarbon solutions.

Oxidation-reduction reactions leading to the formation of free radicals are energetically more advantageous than thermal dissociation. Oxidation-reduction systems, as sources of free radicals, were first investigated for the case of diazoaminobenzene (and hydrogen peroxide) with various reducing agents.

Discussing the reactions in aqueous and aqueous-hydrocarbon media, B. A. Dolgoplosk pointed out that the decomposition of aliphatic-aromatic triazenes under these conditions is brought about by the addition of water, with the quantitative formation of aniline and diazo-hydroxide (Reaction 1). The alkanediazo-hydroxide decomposes with elimination of nitrogen and formation of an alkyl radical and a free hydroxyl (Reaction 2); the radicals formed combine with formation of an alcohol (Reaction 3) or disproportionate with formation of unsaturated compounds (Reaction 4). Reaction 1 is greatly accelerated under the action of dienols, hydroquinone, pyrogallol, ferric sulfate, and other compounds, these substances being unaffected during the decomposition and playing the part of catalysts. In presence of acceptors for free radicals, Reactions 3 and 4 are suppressed. In this system water is utilized for the formation of OH radicals.

The author stated that the inhibiting effect of hydroquinone on chain reactions involving radicals is due to the formation of benzoquinone and stable semiquinone radicals. The reaction between hydroperoxides and hydroquinone in aqueous media may be effectively used for the initiation of radical processes at low temperatures when substances that can reduce quinonoid forms to benzenoid are introduced into the system. This part can be played by sulfites and bisulfites. A system of this type has found industrial application for the initiation of polymerization in an emulsion at a temperature of +5°.

Discussing reactions in hydrocarbon media, B. A. Dolgoplosk stated that oxidation-reduction systems in which peroxides and hydroperoxides take part can be used for the initiation of polymerization in an anhydrous hydrocarbon medium. In absence of monomer, all oxidation-reduction systems cause cross-linking and degradation processes to develop in polymers at low temperatures. Similar effects are shown by various reversible systems containing peroxides, ferric naphthenate, and substances that can reduce ferric iron to ferrous and also by systems containing peroxides and thiols, peroxides and sulfur dioxide, sulfur dioxide and thiols, etc. In the last case sulfur dioxide plays the part of an oxidizing agent. It was stated that various systems containing oxygen which initiate the oxidative degradation of polymers in hydrocarbon media had been studied in detail.

The speaker said that the work had established the possibility in principle of using oxidation-reduction systems for the initiation of chain oxidative processes at low temperatures. The reduction of iron and chromium naphthenates by hydrocarbons can be used for the initiation of polymerization processes at 100°. In these experiments it was shown that the dehydrogenation of a hydrocarbon chain by chromium and iron compounds passes through the stage of free radicals. At 100° various olefins have reducing properties. The decomposition of aliphatic-aromatic triazenes in hydrocarbon media in presence of organic acids proceeds at room temperature with quantitative formation of aniline and formation of an intermediate diazo ester, which then decomposes into acyl and alkyl radicals with formation of nitrogen. In absence of acceptors for free radicals, the reaction proceeds quantitatively in the direction of radical combination, with formation of an ester. In absence of water the reaction can be used for the quantitative alkylation of carboxy and dienol groups (in dihydroxymaleic and ascorbic acids).

Corr. Member Acad. Sci. USSR I. A. Kazarnovsky, S. S. Medvedev, and Academician V. A. Kargin joined in the discussion and pointed out the great importance of this work and its interest for those working on polymerization processes.

A paper entitled "Kinetics and Chemistry of the Polycondensation of Esters of α-Amino Acids" was read by K. T. Poroshin, Doctor Chem. Sci. (co-authors: T. D. Kazarenko and Yu. I. Khurgin). The speaker pointed out the great importance of the synthesis of polymers derived from α-amino acids for the study of natural polypeptides and some of the simple proteins. Synthetic polypeptides provide models for use in the elucidation of the structure of insulin, corticotropine, oxytocin, and vasopressin, and they are widely used in the chromatographic separation of hydrolyzates as models of the corresponding fragments of the protein under investigation. The discovery of physiological activity in some of the poly-α-amino-acids, e. g. polyornithine, polylysine, and polyglutamic acid, and the successful synthesis of these by the polymerization of suitable derivatives show the great importance of developing new, simpler, and more accessible methods for the synthesis of poly-α-amino-acids. The investigation had the object of developing in detail one of the known, but rarely used, methods for the synthesis of polypeptides — the polycondensation of esters of α-amino acids. Glycine ethyl ester, being a convenient object for the study of the polycondensation reaction, was selected for investigation.

The speaker pointed out that the polycondensation process is accompanied by the formation of linear poly-α-amino-acids varying in molecular weight and by the formation also of a six-membered cyclic dimer, 2,5-piperazinedione. The polycondensation reaction can be initiated by carbon dioxide and various other substances. When an exact dosage of initiator is used, reproducible results can be obtained. In order to study the compositions of the polycondensation products, methods were developed for the determination of free monomer, piperazinedione, and the tripeptide.

The variation of the composition of the polycondensation products with time was studied under constant conditions (40°, 2 moles percent of initiator on the amount of monomer). It was found that the rate of formation of piperazinedione was very great in the early stages of the reaction. Simultaneously, linear-polycondensation products accumulated, in the first place tripeptides, which gradually disappeared as the chain grew with formation of products of higher molecular weight. K. T. Poroshin showed that tetrapeptides and still longer peptides are already to be found in the first stage of the reaction. The monomer reacts according to a first-order law. The variation with time of the relative concentration of peperazinedione in the polycondensation products also corresponds to a reaction of the first order. Increase in initiator concentration results in an increase in the reaction rate, and the amount of piperazinedione in the condensation products simultaneously diminishes. As the speaker pointed out, these facts make it possible to advance important hypotheses on the nature of the polycondensation reaction of esters of α-amino acids and the effect of carbon dioxide on the suppression of the cyclization reaction.

Corr. Member Acad. Sci. USSR V. V. Korshak, Doctor Chem. Sci. E. D. Kaverzneva, Academician V. A. Kargin, and others joined in the discussion. Speakers remarked on the significance of the study of the polycondensation of esters of α-amino acids for the eventual synthesis of polypeptides of various structures and for the solution of important biological problems concerned with the relationship between the composition of a compound, the geometric arrangement of various groups in its carbon chain, and its biological activity.

FROM THE CHEMICAL NOMENCLATURE COMMISSION OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R

The Division of Chemical Sciences of the Academy of Sciences of the USSR has set up a Chemical Nomenclature Commission, and this body collects and studies material in various languages on the nomenclature of organic and inorganic compounds with a view to the development of scientific nomenclatures for chemical compounds in the various languages of the peoples of the USSR and their introduction into practice.

The Commission is now working on several schemes of nomenclature, and it is intended to publish these, so that they may be discussed at a conference representing a wide range of interests. This conference is to be held by the Division of Chemical Sciences in the first quarter of 1957, and it is desirable that it should be preceded by extensive informal discussion of the projected schemes.

Among documents of cardinal importance, the Commission has received:

A. Documents on the nomenclature of organic compounds

1) The 1892 Geneva rules and modifications of these introduced in the fourth edition of Beilstein's Handbuch. 2) Rules adopted by the International Union of Pure and Applied Chemistry during 1930-1953. 3) Scheme for the systematic naming of organic compounds in Russian. 4) Scheme for the systematic nomenclature of hydrocarbons and fundamental heterocyclic nuclei (International Union of Pure and Applied Chemistry, 1955). 5) New proposals of Dyson, Taylor, and Patterson for the naming of polycyclic structures (1955).

B. Documents on the nomenclature of inorganic compounds

1) Material discussed by the Nomenclature Commissions of Mendeleev Congresses, compiled by A.Kh. Bork. 2) Rules of the International Union of Pure and Applied Chemistry.

The first three items of Group A were published in "Nomenclature of Organic Compounds" by A.P. Terentyev and others (Acad. Sci. USSR Press, Moscow, 1955). For the first item of Group B see Progr. Chem. 6, 605-621 (in which a detailed bibliography is given), 924, 1251, 1732 (1937). The rest of the material will be published by the Commission.

The Commission invites industrial organizations, research institutes, higher-education establishments, publishers of books and journals, and individual chemists to send in suggestions and comments on matters relating to the nomenclature of organic and inorganic compounds.

Correspondence should be addressed to the Nomenclature Commission, Division of Chemical Sciences, 14 Bolshaya Kaluzhskaya, Moscow, or direct to the chairman of the Commission, A.P. Terentyev, Corresponding Member of the Academy of Sciences of the USSR (Moscow B-234, Chemistry Department, Moscow State University).

Recommendations of the Commission

The Commission recommends that, for Russian publications and for teaching conducted in the Russian language, the names and symbols used for the chemical elements should be those given in the official table (below). This table gives also the values of atomic weights confirmed by the International Commission on Atomic Weights in 1953 and remaining valid for 1956 [Union internationale de Chemie pure et appliquee, Comptes rendus de la XVII Conference. J Am. Chem. Soc. 76, 2033 (1954)].

For some radioactive elements, the mass number of the most stable isotope is given (in square brackets),

TABLE OF THE RUSSIAN NAMES AND SYMBOLS OF THE CHEMICAL ELEMENTS

Name	Symbol	Atomic number	Atomic weight	Name	Symbol	Atomic number	Atomic weight
Azot	N	7	14.008	Neon	Ne	10	20.183
Aktinii	Ac	89	227	Neptunii	Np	93	[237]
Alyuminii	Al	13	26.98	Nikel	Ni	28	58.69
Ameritsii	Am	95	[243]	Niobii	Nb	41	92.91
Argon	Ar	18	39.944	Olovo	Sn	50	118.70
Astatii	At	85	[210]	Osmii	Os	76	190.2
Barii	Ba	56	137.36	Palladii	Pd	46	106.7
Berillii	Be	4	9.013	Platina	Pt	78	195.23
Berklii	Bk	97	[249]	Plutonii	Pu	94	[242]
Bor	B	5	10.82	Polonii	Po	84	210
Brom	Br	35	79.916	Prazeodim	Pr	59	140.92
Vanadii	V	23	50.95	Prometii	Pm	61	[145]
Visnut	Bi	83	209.00	Protaktinii	Pa	91	231
Vodorod	H	1	1.0080	Radii	Ra	88	226.05
Volfram	W	74	183.92	Radon	Rn	86	222
Gadolini	Gd	64	156.9	Renii	Re	75	186.31
Galiii	Ga	31	69.72	Rodii	Rh	45	102.91
Gafnii	Hf	72	178.6	Rtut	Hg	80	200.61
Gelii	He	2	4.003	Rubidii	Rb	37	85.48
Germanii	Ge	32	72.60	Rutenii	Ru	44	101.1
Golmii	Ho	67	164.94	Samarii	Sm	62	150.43
Disprozii	Dy	66	162.46	Svinets	Pb	82	207.21
Evropii	Eu	63	152.0	Selen	Se	34	78.96
Zhelezo	Fe	26	55.85	Sera	S	16	32.066
Zoloto	Au	79	197.0	Serebro	Ag	47	107.880
Indii	In	49	114.76	Skandii	Sc	21	44.96
Iod	J	53	126.91	Strontii	Sr	38	87.63
Iridii	Ir	77	192.2	Surma	Sb	51	121.76
Itterbii	Yb	70	173.04	Talii	Tl	81	204.39
Ittrii	Y	39	88.92	Tantal	Ta	73	180.95
Kadmii	Cd	48	112.41	Tellur	Te	52	127.61
Kalii	K	19	39.100	Terbii	Tb	65	158.93
Kaliforniі	Cf	98	[249]	Tekhnetsii	Tc	43	[99]
Kaltsii	Ca	20	40.08	Titan	Ti	22	47.90
Kislorod	O	8	16	Torii	Th	90	232.05
Kobalt	Co	27	58.94	Tulii	Tu	69	168.94
Kremnii	Si	14	28.09	Uglerod	C	6	12.011
Kripton	Kr	36	83.80	Uran	U	92	238.07
Ksenon	Xe	54	131.3	Fermii	Fm	100	[255]
Kyurii	Cm	96	[245]	Fosfor	P	15	30.975
Lantan	La	57	138.92	Frantsii	Fr	87	[223]
Litii	Li	3	6.940	Ftor	F	9	19.00
Lyutetsii	Lu	71	174.99	Khlor	Cl	17	35.457
Magnii	Mg	12	24.32	Khrom	Cr	24	52.01
Marganets	Mn	25	54.94	Tsezii	Cs	55	132.91
Med	Cu	29	63.54	Tserii	Ce	58	140.13
Mendeleevii	Md	101	[256]	Tsink	Zn	30	65.38
Molibden	Mo	42	95.95	Tsirkonii	Zr	40	91.22
Myshyak	As	33	74.91	Einshteinii	En	99	[253]
Natrii	Na	11	22.991	Erbii	Er	68	167.2
Neodim	Nd	60	144.27				

Publisher's Note: The symbols are as in the original; the names are transliterated. The Consultants Bureau convention of transliterating the Russian letters "i" as "y" at the end of a word has not been followed in this translation.

instead of the atomic weight. These values are derived from data available in the literature on January 1, 1956. Some values confirmed by the International Commission have been altered as follows.

Berkli (berkelium). Previous value 245, half-life 4.95 days. Recommended value 249, half-life 290 days. This is adopted on the basis of the data of Diamond, Magnusson, et al. [Phys. Rev. 94, 1083 (1953); 96, 1576 (1953)].

Kalifornii (californium). Previous value 248, half-life 250 days. Recommended value 249, half-life 470 ± 100 years. This is adopted on the basis of the data of Diamond, Magnusson, et al. [Phys. Rev. 94, 1083 (1953); 96, 1576 (1953)].

The table gives also elements No. 99, 100, and 101, which were obtained in 1951-1955 by Seaborg and others. These investigators proposed the names: No. 99, einshteinii (einsteinium, E); No. 100, fermii (fermium, Fm); No. 101, mendeleevii (mendelevium, Mv) [Phys. Rev. 98, 1518 (1955); Progr. Chem. 25, 133 (1956)].

While accepting these names, the Commission recommends the symbol En for einshteinii (einsteinium) and Md for mendeleevii (mendelevium), in accordance with traditional practice for the derivation of the symbols of the elements.

For isotopes occurring in natural radioactive series — as also for the isotopes of other elements — it is recommended that obsolescent historical names should no longer be used: the symbols given in the official list should be used, and the mass number of the isotope should be indicated by an index.

For isotopes of hydrogen and radon (No. 86) it is permissible to use the following names and symbols when necessary, in addition to those recommended: deiterii (deuterium) D; tritii (tritium) T; aktinon (actinon) An; toron (thoron) Tn.

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PART OF THE FIVE-COMPONENT SYSTEM NICKEL-CHROMIUM-TUNGSTEN-TITANIUM-ALUMINUM

I. I. Kornilov, L. I. Pryakhina and O. V. Ozhimkova

Success in the task of finding new alloys of practical value demands the investigation of the ways in which metals interact in multicomponent systems. Modern technical requirements are most satisfactorily met by alloys of complex chemical composition.

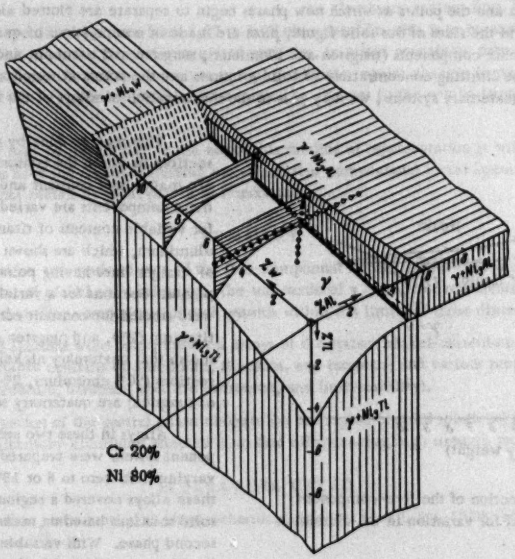

Fig. 1. Phase diagram for part of the five-component system Ni-Cr-W-Ti-Al.

Until recently phase-diagram studies were mainly devoted to binary and ternary metal systems; there have been very few investigations of four-component systems, and only isolated studies of the alloys of five-component and still more complex systems. One of the causes of the lack of progress in this field is the lack of knowledge of methods of investigation of these complex systems and of methods of representing the results on the interaction of metals in the form of phase diagrams. The geometric representation of systems containing more than four components requires that we should pass from three-dimensional measurement to the methods of multi-dimensional

geometry [1], which are less accessible and more difficult to understand than methods of representation within the limits of three-dimensional space. In this connection, we have proposed and described a method of representing parts of multicomponent (more than four components) metal systems within the limits of three dimensions [2]. The application of this method is simplest for metals that tend to give continuous or limited solid solutions with many elements. These metals include many of practical importance, e.g. aluminum, copper, iron, nickel, and titanium. Such systems are of the greatest practical interest.

Using this method, we are making a systematic investigation of metal systems having five, six, and more (up to ten) components.

In this paper we give the results of an investigation of part of the five-component system nickel-chromium-tungsten-titanium-aluminum. The basis for our study of the interactions of these five metals and the construction of a phase diagram of part of the system is provided by experimental material obtained by various authors on the corresponding binary and ternary systems that form part of the five-component system. Following our proposed method of representing the compositions of alloys [2], as our point of origin we took the binary alloy of nickel (80%) and chromium (20%), which is a homogeneous solid solution (Fig. 1). From this point as origin, the contents of the third, fourth, and fifth components (in this case, tungsten, aluminum, and titanium) are plotted along three axes of coordinates (x, y, and z), the chromium content always being constant at 20%. In this way, the compositions in the corresponding sections of ternary systems of nickel, chromium, and third component are plotted along the three axes (x, y, and z) (Fig. 1). On the basis of data in the literature or our experimental data, limiting concentrations of solid solutions and the points at which new phases begin to separate are plotted along these axes. On the planes corresponding to the sides of our solid figure, plots are made of compositions of quaternary alloys of nickel, chromium, and two other components (tungsten and aluminum, tungsten and titanium, and aluminum and titanium). Having determined the limiting concentrations of solid solutions and the points at which new phases begin to separate (Fig. 1) in the quaternary systems, we may pass to the investigation of alloys of the five-component system.

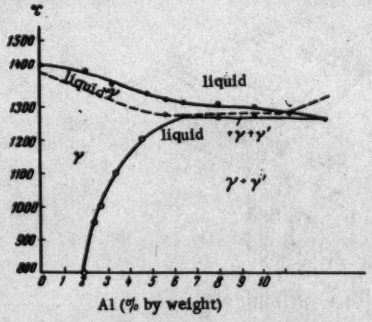

Fig. 2. Polythermal section of the five-component system Ni-Cr-W-Ti-Al for variation in the aluminum content.

This may be done by considering suitable sections in which the contents of some components are maintained constant and the contents of one or more components are varied. We studied sections for variable contents of titanium, tungsten, and aluminum, which are shown in Fig. 1, in the form of straight lines having points on the corresponding planes. Sections for a variable content of aluminum were studied for constant contents of chromium (20%), titanium (2%), and tungsten (6% and 9%). It was first shown that quaternary nickel alloys in these two sections (20% chromium, 2% titanium, and 6 or 9% of tungsten) are quaternary solid solutions.

Alloys in these two sections of the five-component system were prepared with aluminum contents varying from zero to 8 or 16%. The compositions of these alloys covered a region of five-component solid solutions based on nickel with separation of a second phase. With variable aluminum content and limiting saturation with aluminum, the basis of the separating phase was a nickel-aluminum compound – very probably Ni_3Al. If we assume that the compound Ni_3Al is able to dissolve excess of nickel and, to some extent, chromium, tungsten, and titanium, it may be considered that in this phase all these elements will be present in the form of solid solutions in the compound Ni_3Al.

A series of polythermal sections was constructed for alloys of the system Ni-Cr-W-Ti-Al, and some of the properties of the alloys were studied (microstructure, hardness, specific resistance, and heat-resistance). By way of example, in Fig. 2 we give one of our polythermal sections for alloys of variable aluminum content and constant contents of chromium (20%), tungsten (9%), and titanium (2%).

In this figure we have constructed from our own data the fusion diagram for alloys of this section and the

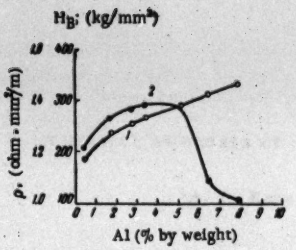

Fig. 3. Composition-property diagram of alloys of the system Ni-Cr-W-Ti-Al having a variable aluminum content: 1) hardness of alloys after aging at 700° for 100 hours; 2) electrical resistance at 20°.

solubility-temperature curve for aluminum, determined by the method of microstructure analysis. As will be seen from the diagram, in the five-component alloys addition of aluminum brings about a lowering of the liquidus curve. At aluminum contents of more than 7-8%, a second halt occurs on the cooling curves, possibly corresponding to crystallization of the eutectic. Fig. 3 shows curves for the variation of hardness (1) and of specific resistance (2) for alloys tempered from 1150° and aged at 700° for 100 hours.

With increase in the aluminum content, the hardness of the alloys increases continuously from 185 to 328 kg/mm². With increase in the aluminum content from 0.5 to 2.8%, the specific resistance of the alloys increases from 1.22 to 1.35 ohm mm²/m and has a maximum of 1.37 ohm mm²/m at an aluminum content of 3.4-5.1%. Further increase in the aluminum content from 5.1 to 7.9% causes a sharp reduction in the specific resistance from 1.37 to 1.02 ohm mm²/m; this is to be explained by the appearance of a second phase, which takes the form of coagulated particles, in alloys containing more than 5% of aluminum. Hence, the hardness and specific resistance curves in Fig. 3 indicate regular changes in properties, which, as in the case of binary and tertiary systems [3-5], can be related to changes in the compositions and phase structures of the alloys.

In conclusion it may be stated that by the use of this method of representation it will be possible to investigate partial phase diagrams of many complex (having more than four components) metal systems, based not only on nickel, but also on other metals of great practical importance.

SUMMARY

1. An investigation was made of part of the five-component system nickel-chromium-tungsten-titanium-aluminum in the region of nickel solid solutions. Use was made of a method of representing parts of multicomponent (having more than four components) metal systems within the limits of three dimensions.

2. Polythermal sections were constructed for alloys of the system nickel-chromium-tungsten-titanium-aluminum having variable contents of aluminum, titanium, and tungsten; and various properties of these alloys were studied (microstructure, hardness, specific resistance, and heat-stability).

3. The investigation of the partial phase diagram (in the region of solid solutions) of the system nickel-chromium-tungsten-titanium-aluminum enabled us to find alloys having high strength properties.

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THERMAL ANALYSIS OF THE SYSTEM BENZENE-STANNIC BROMIDE

A. F. Kapustinsky and Yu. M. Kessler

Kapustinsky and Drakin [1,2] have previously studied some systems consisting of benzene and halogen-substituted methanes, and they have advanced some views on the chemistry of the formation of compounds in these systems and the structures of these compounds, the formation of compounds between benzene and carbon tetrahalides being explained by the unsaturated character of halogens in tetrahalides and the presence of three oscillating double bonds in the benzene molecule. Confirmation of this view can be found in recently published work by Andrews [3]. Kapustinsky and Drakin [1,2] found that the possibility of compound formation diminishes as the size of the tetrahalide molecule increases, this effect being attributed to steric hindrance.

Stannic halides are analogous in structure to carbon tetrahalides, i.e., the molecule has the form of a regular tetrahedron having a tin atom in the center. However, tin is more electropositive than carbon, and the halogens in stannic halides should therefore be more saturated than those in the corresponding carbon tetrahalides. Also, the size of a stannic halide molecule is considerably greater than that of the corresponding carbon tetrahalide molecule, in fact the size of the molecule of the most compact stannic halide - stannic chloride (we have no data for stannic fluoride) – is greater than that of the carbon tetraiodide molecule: the Sn - Cl distance is 2.30 A, whereas the C-I distance is 2.12 A [4]. On the basis of these considerations and the nature and structure of crystalline benzene-addition compounds, as described in the papers cited [1,2], we may expect that benzene will not form compounds with stannic halides.

Actually, with benzene, stannic chloride forms a system having a simple eutectic [5]. This result is in accord with data on other properties of this system. Absence of chemical interaction between the components is indicated by the viscosity isotherms, determined at 25° and 70° [6]. The refractive index shows a feeble positive departure from additivity [7]. The vapor pressures of mixtures show only very slight departures from Raoult's law [8]. Schultze and Hock found that mixing of the components was accompanied by appreciable cooling and increase in volume and that positive departures of the vapor pressures of mixtures from Raoult's law increase as the temperature falls (measurements were made at 30°, 100°, and 125°) [9].

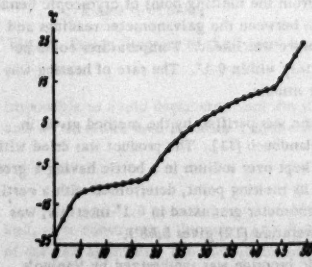

Fig. 1. Heating curve for a mixture containing 72.2 moles % of $SnBr_4$.

EXPERIMENTAL

For the construction of fusion diagrams of the system benzene-$SnBr_4$ we determined heating curves of mixtures by the method of constant temperature differences. This method, wich was devised by Kapustinsky and Barsky [10] for the determination of heat capacities and heats of reactions and transformations, was more suitable for our purpose than other methods, since the heating curves obtained by this method are more prolonged and have more clearly defined horizontal sections corresponding to isothermal effects and more clearly defined points of inflection at the termination of non-isothermal effects than those found on heating curves obtained by other methods.

The curves are completely reproducible. This ensures that the determination of the transformation temperatures will be reliable. A typical heating curve for our mixtures is given in Fig. 1. We are the first to use this method for the study of fusion diagrams.

The apparatus in which the freezing and subsequent heating of the samples were carried out is shown in Fig. 2. It consists of a thin-walled brass jacket 1, which serves for the better equalization of the temperature over the height of the vessel containing the sample, the glass test tube 2. The test tube is fixed in the stopper 3, which is held in the neck of the jacket 1. The tube is further centered by means of the Plexiglas ring 4, which is cemented to the inside of the jacket. The ring 4 serves also as a support for the differential thermopile 5, which consists of 13 pairs of copper-constantan junctions arranged at various heights around the circumference of the test tube. In this way a constant temperature difference is maintained between the inner surface of the jacket 1 and the outer surface of the test tube 2; the standard envelope regulating the inflow of heat is the layer of air, about 5 mm in the thickness, between these two surfaces. The test tube is firmly closed by the stopper 6, which carries the holder 7 for the capillary jacket 8 of the simple copper-constantan couple 9. This holder serves also as a guide for the electromagnetic reciprocating platinum-ring stirrer 10, which is operated from the coil 11 mounted directly on the test tube; the stirrer works at three periods per second. For heating, this apparatus is placed in a Dewar vessel, in which it is supported by the stopper 3. The Dewar vessel contains an open heating element of nickeline wire (diameter 0.15 mm, 10 turns/cm on a special mounting consisting of six copper rods covered with insulating lacquer and fixed cylinder-fashion by means of Plexiglas rings).

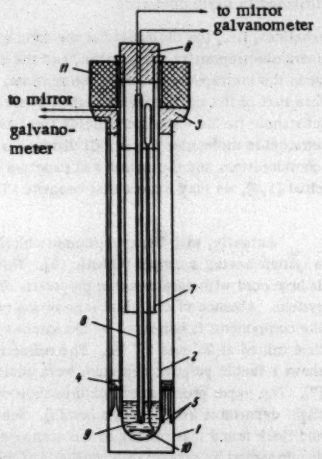

Fig. 2. Apparatus for the determination of heating curves.

Checks for constant difference were carried out continuously from the readings of a mirror galvanometer, and readings of simple and differential galvanometers were made every 30 seconds at the signal from a buzzer working from a Warren SD-2 motor. The heating was regulated with three rheostats of resistance 260, 2000, and 4000 ohm, and, for a heater resistance of 1100 ohm, it was then possible to maintain a constant difference accurately within 0.5%.

The calibration curve of the simple galvanometer was constructed from the transformation temperature and melting point of Kahlbaum carbon tetrachloride, which was dried further with amalgamated aluminum, from the melting point of ice from doubly distilled water, and from the melting point of cryoscopic benzene. The relation between the galvanometer readings and the temperature was linear. Temperatures could be read accurately within 0.1°. The rate of heating was 1.5-1.8° per minute.

Benzene was purified by the method given in Beilstein's Handbuch [11]. The product was dried with sodium and kept over sodium in a bottle having a ground-in stopper. Its melting point, determined with a certified normal thermometer graduated in 0.1° intervals, was 5.58° (the literature [12] gives 5.58°).

Stannic bromide was synthesized by Vanino's method [13] from Kahlbaum tin and "pure grade" liquid bromine. The product was distilled twice from a Wurtz flask having a receiver adapter directly attached to the outlet through a ground joint. It was kept in a flask with a ground-in stopper in a desiccator over calcium chloride. The purity of the product was established from its melting point, which was determined directly in our apparatus: the value found was 29.40° (the literature [14] gives 29.45°).

The mixtures were prepared directly in the test tube with exclusion of moisture. All weighings were carried out accurately within 0.0001 g on a microanalytical balance. The fusion diagram that we obtained is shown in Fig. 3. It will be seen that no compounds are formed between the components. The eutectic is at a point

corresponding to 9.9° and 65.9 moles % of benzene. On the heating curves of mixtures containing 87.4, 88.0, and 94.8% of stannic bromide, halts were noted at 15.7°, 15.6°, and 15.3°, respectively. On the heating curve of pure stannic bromide there is also a halt at 15.3°. At this temperature the liquidus curve has a point of inflection. This behavior indicates that stannic bromide undergoes a polymorphous transformation at 15.3°.

In the literature there is only one reference to the existence of two modifications of stannic bromide. Biltz and Jeep [15], in a study of the system $SnBr_4$ – bromine by the thermoanalysis method, observed halts on the heating curves of mixtures rich in stannic bromide at −6° and an inflection at this temperature on the corresponding branch of the liquidus, but on the heating curves of the pure substance they obtained only one halt, which corresponded to melting. Biltz and Jeep observed the transformation in pure stannic bromide visually – by the change in the appearance of the crystals when cooled – and dilatometrically – by the reduction in volume between −6° and −7°.

The results of our experiments indicate the absence of any transformation in the neighborhood of −6°, both in the pure substance, and also in its mixtures with benzene. When we consider that, on one hand a transformation occurring with change in the appearance of the crystals and a considerable change in volume must be accompanied by an appreciable thermal effect, which could not remain undetected at the sensitivity characteristic of our method, and, on the other hand, we did not succeed in observing any change in the appearance of the crystals at −6°, either in the heating, or in the cooling of stannic bromide, although we did observe such a change at about 15° we are compelled to regard the results of Biltz and Jeep as erroneous. It should be noted also that on the liquidus branch of stannic bromide as studied by de Carli [16] in the system $SnBr_4$-nitrobenzene (simple eutectic) there is an inflection at about 18°, for which the author gives no explanation.

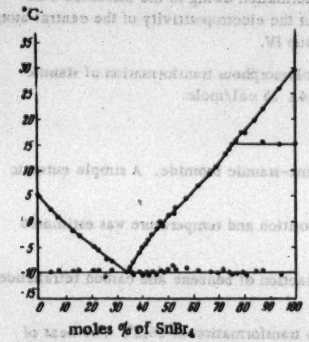

Fig. 3. Fusion diagram of the system benzene-$SnBr_4$.

The establishing of a simple eutectic from the fusion diagram does not in itself make it possible to estimate the interaction between molecules of the components. This can be done by determining the heat of mixing. The method of thermoanalysis that we used enabled us to determine the heats of isothermal processes directly from the heating curves of mixtures with a probable error of not more than 5% by use of the following equation [10]:

$$Q = \frac{k}{m} \Delta t \Delta z, \qquad (1)$$

in which Q is the thermal effect, k is the coefficient of heat transfer, Δt is the temperature difference as determined by the readings of the differential galvanometer, Δz is the duration of the halt, and m is the mass of the sample. From this equation we determined the heat of mixing of the components at the eutectic temperature. With the simplified arrangement for regulating the heating which we used in these experiments, it was impossible to avoid departures from the standard value of the difference at the beginning and at the end of a halt, and we therefore used Equation 1 in the form:

$$Q = \frac{k}{m} \int_1^2 \Delta t \, dz, \qquad (2)$$

and, after constructing the curve $\Delta t = f(z)$, we determined the integral graphically, taking the beginning and end of the halt as limits. The coefficient of heat transfer k was determined from the heats of fusion of stannic bromide, cyclohexane, nitrobenzene, and benzene. The maximum departure from the average value was 3.7%. As the investigated range of temperatures was only 40° and the maximum departure of the difference from the standard value was not greater than 20% and occurred for only short times in comparison with the duration of the halts, we neglected the variation of k with temperature.

The heat of fusion of the eutectic Q may be represented as the sum of the heats of fusion of the components ΔH_A and ΔH_B and the heat of mixing them Q_m:

$$Q = n_A \Delta H_A + n_B \Delta H_B + Q_{cm}, \qquad (3)$$

in which n is the number of moles of the given component in a mixture of eutectic composition. In view of the absence of data in the literature on the heat capacity of stannic bromide in the liquid state, we took the heats of fusion of the pure components for our calculation. In view of the small temperature range, the error introduced was less than the experimental error; its effect would be to make the determined value too low, for in our case $(cp)_l - (cp)_s > 0$ for both components. The value of Q_m was determined as the mean of 22 determinations for mixtures on both sides of the eutectic. Q_m was found to be a quantity having about one-tenth the value of Q, so that an error of 5% in the determination of Q will result in a 50% error in the determination of Q_m. Hence, we can speak with confidence only of the order of Q_m. We obtained the value of $Q_m = 256 \pm 125$ cal per mole of mixture, which indicates absence of chemical interaction. When we compare this value with the almost temperature-independent heat of mixing of carbon tetrachloride and cyclohexane (35.5 cal per mole of mixture at 20° [17]), between which there are also no compounds formed, it becomes obvious that not even signs of chemical affinity between benzene and stannic bromide molecules are to be found. Hence, the behavior of stannic halides in mixtures with benzene falls within the scope of the concepts discussed above, and it may be considered that these are valid for all the tetrahalides of Group IV.

Actually, with increase in the size of the tetrahalide molecule, the formation of a compound by the orientation of three halogens of the molecule toward the three double bonds of the benzene molecule becomes impossible on geometric grounds. Moreover, the orientation of a tetrahalide molecule with one halogen atom associated with a double bond of benzene cannot result in compound formation owing to the increased electrosaturation of the halogens, a property that increases with increase in the electropositivity of the central atom of the tetrahalide as we pass from carbon to the other elements of Group IV.

By the same method we have determined also the heat of the polymorphous transformation of stannic bromide at 15.3° ($[SnBr_4]_I \rightleftharpoons [SnBr_4]_{II}$), which we found to be $\Delta H = 304 \pm 15$ cal/mole.

SUMMARY

1. A study was made of the fusion diagram of the system benzene-stannic bromide. A simple eutectic was established at −9.9° and 34.1 moles percent of stannic bromide.

2. The heat of mixing of the components at the eutectic composition and temperature was estimated and found to be 256 ± 125 cal per mole of mixture.

3. It was shown that structural concepts which explain the interaction of benzene and carbon tetrahalides are applicable also to binary systems of benzene and stannic halides.

4. It was shown that stannic bromide undergoes a polymorphous transformation at 15.3°. The heat of transformation was determined and found to be 304 ± 15 cal/mole.

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SOLUBILITY OF SILICIC ACID

Yu. V. Morachevsky and M. M. Piryutko

The first investigation on the solubility of silicic acid was carried out more than one hundred years ago by Fuchs [1]. The matter was reexamined subsequently by various investigators, and an indication of the results obtained is given in Table 1.

TABLE 1

Author	Year	Value of solubility found ($g/ml\ SiO_2$)	Temperature of solution	Attainment of equilibrium	Form of material investigated	Method of determining concentration of silicic acid in solution
Fuchs [1]	1852	$13 \cdot 10^{-3}$	Not stated	Not stated	Gel	Gravimetric
Maschke [2]	1855	$90 \cdot 10^{-3}$	"	"	"	"
Struckman [3]	1855	$21 \cdot 10^{-3}$	"	"	"	"
Graham [4]	1864	$10—20 \cdot 10^{-3}$	"	"	"	"
Seeman [5]	1905	$7.7 \cdot 10^{-3}$	18°	"	"	"
		$27 \cdot 10^{-3}$	100°	"	"	"
Lenher and Merrill [6]	1917	$16.1 \cdot 10^{-3}$	25°	Equilibrium	"	"
		$42.7 \cdot 10^{-3}$	90°	"	"	"
Antipov-Karataev and Ryub [7]	1936	$12.3 \cdot 10^{-3}$	Room temp.	"	"	Colorimetric
Correns [8]	1940	$24 \cdot 10^{-3}$	"	"	"	Gravimetric
Alexander [9]	1954	$10—14 \cdot 10^{-3}$	25°	"	"	Colorimetric

As will be seen from Table 1, the results of different authors vary considerably. The probable causes of this are insufficient attention to the attainment of equilibrium between the phases and to other experimental conditions (temperature, nature of the material) and insufficient attention to the form in which the silicic acid passes into solution. The gravimetric method of determining the concentration gives the overall silicic acid content, irrespective of the form in which it occurs in the solution, and it therefore does not enable us to distinguish clearly between true dissolution of silicic acid and its passage into solution as the result of the peptization of a gel. The process is complicated by the polymerization of silicic acid during its treatment with water. The colorimetric method determines the content of only a relatively small amount of the polymerized form of silicic acid (it determines only the component known as the α-form in Egorova's classification [10]).

Many investigations have been reported on the passage of silicic acid into solution (leaching) when various silicates are treated with water or various aqueous solutions. Such passage of silicic acid into solution is often incorrectly referred to as its solubility. We shall not cite this literature because these investigations do not characterize the solubility of silicic acid, solid phase being not silicic acid, but always a silicate of some kind, or quartz.

The question of the solubility of silicic acid in water and dilute solutions of certain salts has recently attracted great interest in connection with hydroconstruction. In various cases it is of practical importance to establish the limiting concentration of silicic acid in water and in salt solutions of various composition. For example, such data are essential for the calculation of the limiting rate of removal of silicic acid in true solution from rocks through which waters of some particular composition are filtering. The present paper gives the results of an investigation of the solubility in pure water of a silicic acid gel prepared in various ways and dehydrated to various degrees.

EXPERIMENTAL

1. Solubility of Silicic Acid Gels Dried at Room Temperature

Experimental Procedure. Silicic acid gels prepared by two methods were investigated.

Gel "a" was prepared by decomposing sodium silicate with acid. Pure silica was fused with six times its weight of sodium carbonate. The product was decomposed with dilute hydrochloric acid, the solution was evaporated to dryness, and the residue was moistened with hydrochloric acid and leached with water. The silicic acid gel so obtained was washed with hot water on a Buchner funnel until the washings were free from chloride ion. It was dried in the air at room temperature and kept in a jar having a ground-in stopper. Analysis of gel "a" gave the following results: SiO_2 – 77.52%; H_2O – 22.42%; impurities – 0.06%.

Gel "b" was prepared by hydrolyzing freshly distilled silicon tetrachloride. After the hydrolysis the solution was evaporated to dryness and the residue was given the treatment described above. Analysis of gel "b" gave the following results: SiO_2 – 66.72%; H_2O – 33.26%; impurities – 0.02%. Gel "b", therefore, was considerably more hydrated than gel "a". Also, whereas gel "a" was a light powder, gel "b" was a much denser product.

The solubility determination was carried out as follows.

Distilled water (200 ml) was poured on a sample of the gel (corresponding in weight to 1 g of anhydrous silica) contained in a stainless-steel beaker. The beaker was contained in a water thermostat maintained at 25.9 ± 0.2° by means of a thermoregulator; the thermostat and beaker were provided with stirrers. Stirring was continued for eight hours, after which the thermostat and stirrer were switched off until the next morning, when they were switched on again for eight hours, and so on. The temperature of the solution fell somewhat during the breaks.

Samples for the determination of the silicic acid concentration were taken at set intervals and always after a long period of stirring at 25.9°. The samples were taken by pipet through a No. 3 porous glass filter with the aid of a water pump. Two test samples were taken: one for the determination of the α-form (silicate ions that are not polymerized or only slightly polymerized), and another for the determination of the silicic acid present both as simple and as highly polymerized ions that no longer give a color with molybdic acid. Simple calculation gave the contents of both of the forms of silicic acid that were of interest to us.

For the silicic acid that could be determined colorimetrically, 2 ml of the solution was diluted with water in a 25-ml measuring flask and acidified by the addition of 0.6 ml of 4 N HCl; 1 ml of 10% ammonium molybdate solution was then added, and the solution was diluted with water to the 25-ml mark. The solution was stirred for 15-20 minutes, and the intensity of the yellow color was then determined with the aid of an FEK-M photoelectric colorimeter.

For the total content of silicic acid, 2 ml of the solution was placed in a tall platinum thimble and diluted to about 10 ml; 1 ml of 3 N Na_2CO_3 was added. The solution was heated for 5-10 minutes in a boiling water bath; this resulted in the depolymerization of the silicic acid and its conversion into a form capable of giving a colored compound with molybdic acid. The solution was cooled, acidified with 1.4 ml of 4 N HCl, and transferred to a 25-ml measuring flask. Ammonium molybdate was added, the solution was made up to volume, and the colorimetric determination was carried out as above.

Results for Solubility of Silicic Acid at 25.9°. The results of the solubility experiments on the silicic acid gels "a" and "b" are given in Table 2. The total concentration of silicic acid and the concentration of colorimetrically determinable silicic acid (α-form) are given in separate columns.

It follows from Table 2 that 1) almost the whole of the silicic acid in the solution is in the α-form, i.e., in the form of simple ions that give a colored heteropoly acid with molybdic acid, the observed differences being within the limits of experimental error; 2) the equilibrium solubility of silicic acid gel does not depend on the method by which it is prepared and has an average value of $12.5 \cdot 10^{-5}$ g/ml SiO_2; 3) the method of preparation affects only the rate of dissolution, equilibrium being attained considerably more rapidly for the gel "b" than for the gel "a".

Results for the Solubility of Silicic Acid at 97°. The only difference in the experimental procedure was that the dissolution was carried out in a silver beaker and the temperature of the thermostat was maintained

at 97 ± 0.5°. The solution was stirred continuously; as the rate of dissolution increases rapidly with rise of temperature, experiments could be completed within one day without breaks. The results are given in Table 3.

These results show that equilibrium is attained at 97° within two hours. The equilibrium solubility is $41.5 \cdot 10^{-5}$ g/ml SiO_2. It is notable that in the hot solution the whole of the silicic acid is in the α-form.

TABLE 2

Duration of experiment in hours (the figure in parenthesis is the number of hours during which the solution was stirred)	Concentration of silicic acid (10^{-5} g/ml SiO_2)			
	Gel "a"		Gel "b"	
	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form
6 (6)	2.6	2.6	3.6	3.4
30 (14)	7.6	7.0	9.2	8.9
54 (22)	9.5	9.2	11.0	10.5
78 (31)	11.2	10.5	12.2	12.2
102 (39)	11.0	11.0	—	12.6
150 (47)	13.0	11.8	13.1	12.5
198 (63)	12.8	11.8	13.0	13.0
246 (79)	12.4	12.2	12.4	12.5
342 (103)	12.0	11.8	12.8	13.2
438 (135)	12.8	12.6	12.8	13.2
534 (159)	12.5	12.5	12.8	12.5

TABLE 3

Duration of experiment (hours)	Concentration of silicic acid (10^{-5} g/ml SiO_2)			
	Gel "a"		Gel "b"	
	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form
0.5	27.5	27.8	30.5	30.8
1.0	38.0	38.0	39.0	39.0
2.0	—	42.2	41.5	42.0
3.0	43.0	42.5	40.5	42.0
4	42.5	41.3	41.3	41.5
5	41.3	41.3	41.0	41.0
6	42.5	41.3	—	41.3
7	—	41.3	41.0	41.3

The hot saturated solution of silicic acid was allowed to cool and then left at room temperature (18-20°). Periodically, it was stirred and test samples were taken for the determination of silicic acid concentration. The results of these experiments are shown in Table 4.

As Table 4 shows, when a solution saturated at 97° is cooled, the concentration of silicic acid gradually falls and finally attains a value close to that obtained previously at 25.9°, i.e., $11.0 \cdot 10^{-5}$ g/ml SiO_2. This value is a little lower than that obtained at 25.9° ($12.5 \cdot 10^{-5}$ g/ml), which is readily explained by the lower temperature to which the solution was cooled. It is very interesting that the whole of the silicic acid is in the form of simple colorimetrically determinable particles. Hence, when a solution, saturated at 97°, is cooled, silicic acid is precipitated from the solution into the solid phase; only the amount corresponding to the solubility at the given temperature remains in solution. It should be noted that, in the process of cooling, the solution corresponding to the gel "b" passes more rapidly into a state of equilibrium than the solution corresponding to the gel "a".

Experiments were carried out on the evaporation of a saturated solution of silicic acid at 97°. When the evaporation was carried out without the removal of the solid phase (gel), only in the first minutes was increase in silicic acid concentration (supersaturation) observed, and, if evaporation was stopped and the solution maintained

TABLE 4

Time (hours) from end of heating to taking of sample	Concentration of silicic acid (10^{-5} g/ml SiO_2)			
	Gel "a"		Gel "b"	
	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form
18	32.5	32.5	26.0	26.0
45	—	—	19.2	19.5
67	26.2	26.2	15.2	15.2
91	22.0	22.0	—	—
115	—	—	13.5	13.5
139	19.8	19.2	12.8	12.8
187	18.0	17.0	13.5	13.5
235	15.8	15.3	12.8	12.8
331	14.5	14.5	12.0	12.0
475	—	—	11.0	10.8
499	13.0	12.8	—	—
739	13.2	12.5	12.0	11.5
1003	12.2	12.0	10.8	10.8
1459	11.2	10.8	10.8	10.5
2419	11.0	10.8	—	—

TABLE 5

Time of keeping (hours)	Concentration of silicic acid (10^{-5} g/ml SiO_2)	
	Total	Colorimetrically determinable form
—	47.5	46.5
18	45.5	24.2
92	47.0	16.5
216	45.0	14.0
379	47.0	12.5
668	47.0	12.2
885	45.8	11.8
1101	45.2	12.2

at the same temperature, the silicic acid concentration fell until, after one hour, it attained the equilibrium value corresponding to the given temperature, i.e., 97°. When, after saturation at 97°, the solid phase was removed, it was found to be possible greatly to increase the silicic acid concentration without precipitation of a solid phase or even visible turbidity in the solution. It was found that in this case most of the silicic acid was in the form that is not determinable colorimetrically, i.e., in the form of relatively highly polymerized particles, possibly attaining the size of colloidal particles. Thus, for a total silicic acid content of $113 \cdot 10^{-5}$ g/ml SiO_2 we found only $17.5 \cdot 10^{-5}$ g/ml colorimetrically, $95.5 \cdot 10^{-5}$ g/ml being more highly polymerized (β- and perhaps also some γ-silicic acid, as described in Egorova's classification).

It was considered to be of interest also to carry out an experiment on the cooling of a solution saturated at 97°, the solid phase being first removed. This experiment gave the results given in Table 5. It will be seen that, as a solution saturated with silicic acid at 97° is kept in absence of solid phase, the concentration of simple particles (α-form) falls toward the equilibrium solubility for the given temperature, whereas the total silicic acid content of the solution remains almost constant, i.e., much of the silicic acid is present in the solution in the form of more highly polymerized, possibly colloidal, particles.

In the next series of experiments, 400 ml of water was heated with the gel "b" for three hours. The solution, saturated at 97°, was separated from the solid phase and divided into five parts, each of which was kept in a flask coated on the inside with paraffin wax. Some silicic acid gel was introduced into the first flask immediately. Gel was introduced into the second after 67 hours, into the third after 140 hours, and into the fourth after 188 hours; no solid phase was introduced into the fifth flask. Test samples were taken from all these solutions periodically, and both forms of silicic acid were determined. The results of this series of experiments are given in Table 6.

The following conclusions can be drawn from these experiments. 1) In absence of solid phase there is a slow fall in the concentration of simple forms of silicic acid, which tends to its equilibrium value, while the total silicic acid content of the solution remains almost constant; this confirms the results of the experiment described above (Table 5). 2) Introduction of solid phase (gel) into the solution accelerates the lowering of the concentration of simple forms of silicic acid and causes also a gradual fall in the total silicic acid concentration, i.e., a gradual

TABLE 6

Time of standing (hours)	Concentration of silicic acid (10^{-5} g/ml SiO_2)									
	Solution 1		Solution 2		Solution 3		Solution 4		Solution 5	
	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form	Total	Colorimetrically determinable form
0	40.8	40.8	40.8	40.8	40.8	40.8	40.8	40.8	40.8	40.8
	Solid phase added		—	—	—	—	—	—	—	—
18	28.8	28.5	40.5	38.0	40.5	38.0	40.5	38.0	40.5	38.0
67	19.2	18.0	40.5	22.5	39.5	28.5	39.5	22.5	39.5	22.5
	—	—	Solid phase added		—	—	—	—	—	—
91	16.5	16.0	38.5	18.8	41.8	20.0	41.8	20.0	41.8	20.0
140	14.8	14.2	34.5	13.8	41.8	16.5	41.8	16.5	41.8	16.5
	—	—	—	—	Solid phase added		—	—	—	—
188	13.5	13.5	33.0	12.8	39.6	14.0	40.2	15.2	40.2	15.5
	—	—	—	—	—	—	Solid phase added		—	—
281	13.2	13.2	33.0	—	36.8	12.5	38.0	12.5	40.8	14.2
430	12.5	12.0	30.2	11.5	34.2	11.2	36.8	11.2	41.8	13.2
672	11.5	11.0	29.8	10.8	33.5	11.2	34.2	11.0	41.5	13.0
1182	11.0	10.8	28.0	10.8	31.8	10.8	32.0	10.8	41.5	12.5
1872	10.8	10.8	25.8	10.8	30.0	10.8	30.0	10.8	40.8	11.8
2376	10.0	10.5	21.2	10.8	24.3	10.5	25.0	10.2	40.8	11.8
5088*	9.0	9.2	16.0	9.2	17.0	9.2	18.0	9.5	—	11.2
5832*	9.0	9.2	13.5	9.0	16.0	9.2	17.8	9.2	40.5	10.8

* Room temperature was 15-16°.

passage of highly polymerized forms into the precipitate.

Hence, in a solution in equilibrium with a silicic acid gel there are only very simple silicic acid particles that are able to react with molybdic acid; the concentration of these particles depends on the temperature. Solutions of higher silicic acid content can be prepared 1) by the evaporation of solutions not containing solid phase, or 2) by the cooling of solutions that have been saturated at a higher temperature and then separated from the solid phase. These solutions of higher silicic acid content contain simple particles at a concentration corresponding to the solubility and more complex, more highly polymerized particles, the concentration of which can be so high in absence of solid phase that it cannot be referred to as the saturation concentration.

2. Solubility of Silicic Acid Dehydrated to a Varied Extent

In order to determine the effect of the water content of the gel and of its preliminary thermal treatment on the solubility of silicic acid, gels "a" and "b" were maintained at a given temperature – varying from 100° to 1120° in different experiments – until constant weight was attained. The effects of these treatments on the extent of the dehydration of the gel are shown in Table 7.

The treated gel was placed in a beaker containing water at 25.9°, and the subsequent procedure was identical with that described above. In these experiments the solid phase was silicon dioxide hydrated to various extents, and the process of its passage into solution had to proceed via a hydration stage.

The experiments showed that, when silicic acid dried at 105° or calcined at 200, 500, 800, 900, or 1000° was treated with water, silicic acid gradually passed into solution; moreover, 1) the equilibrium concentration was the same as that found for the air-dried gel, i.e., $12.5 \cdot 10^{-5}$ g/ml SiO_2 at 25.9°; 2) all the silicic acid passing into solution was in the form of simple particles, capable of reacting with molybdic acid; 3) the rate of dissolution was lower the higher the calcination temperature of the gel, i.e., the lower the water content of the calcined material. Thus, for the gel dried at 105°, the equilibrium silicic acid concentration was attained in the solution

TABLE 7

No.	Composition / Treatment conditions	Gel "a"			Gel "b"		
		SiO_2	H_2O	Formula	SiO_2	H_2O	Formula
1	Dried in the air at room temperature	77.52	22.42	$SiO_2 \cdot H_2O$	66.72	33.26	$SiO_2 \cdot 1.7H_2O$
2	Dried at 105°	95.33	4.67	$6.1\,SiO_2 \cdot H_2O$	95.80	4.20	$6.8\,SiO_2 \cdot H_2O$
3	" 200°	96.74	3.26	$9.2\,SiO_2 \cdot H_2O$	96.76	3.24	$9.2\,SiO_2 \cdot H_2O$
4	Calcined at 500°	99.13	0.87	$34.5\,SiO_2 \cdot H_2O$	98.68	1.32	$22.5\,SiO_2 \cdot H_2O$
5	" 800°	99.64	0.36	$83\,SiO_2 \cdot H_2O$	99.32	0.68	$43.6\,SiO_2 \cdot H_2O$
6	" 900°	99.75	0.25	$119\,SiO_2 \cdot H_2O$	99.30	0.70	$43.6\,SiO_2 \cdot H_2O$
7	" 1000°	100	—	SiO_2	99.84	0.16	$185\,SiO_2 \cdot H_2O$
8	" 1120°	100	—	SiO_2	100	—	SiO_2

under our experimental conditions in 125 hours, whereas for the gel calcined at 900° the equilibrium concentration was attained only after 816 hours, and for the gel calcined at 1000° the silicic acid concentration attained only $10 \cdot 10^{-5}$ g/ml SiO_2, i.e., somewhat lower than that attained for gels calcined at a lower temperature, even after 1824 hours; in all cases, for the gel "b" equilibrium solubility was attained more rapidly than for gel "a".

The gel calcined at 1120° was found by analysis to be quite free from water, and it differed greatly from the others with respect to solubility. For this form of silica the amount that passed into solution was negligibly small. A sample was placed in water in a stainless-steel beaker and left at room temperature with periodic stirring for 7128 hours. For the gel "a" the silicic acid concentration was then only $0.1 \cdot 10^{-5}$ g/ml SiO_2, and for the gel "b" it was only $0.6 \cdot 10^{-5}$ g/ml SiO_2.

SUMMARY

1. The solubilities of silicic acid gels in water at 25.9° and 97° were studied.

2. It was shown that the silicic acid that passed into solution was present entirely in the form of simple molecules and ions capable of reacting with molybdic acid. The equilibrium concentration was attained slowly at 25° ($12.5 \cdot 10^{-5}$ g/ml SiO_2) and rapidly at 97° ($41.5 \cdot 10^{-5}$ g/ml SiO_2).

3. A study was made of the behavior of silicic acid during the evaporation of its solutions and during the cooling of solutions saturated at 97°.

4. A study was made of the effect of prior heat treatment of a silicic acid gel on its solubility. It was shown that prior heating at 100, 200, 500, 800, or 900° has no effect on the solubility of silicic acid, but the rate of dissolution falls as the temperature of the previous heat treatment is raised. The solubility of silicic acid calcined at 1120° is very greatly reduced.

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REACTION BETWEEN THE ETHER COMPLEX OF BORON TRIFLUORIDE AND LITHIUM HYDRIDE

COMMUNICATION 1. PREPARATION OF PURE DIBORANE

V. I. Mikheeva and E. M. Fedneva

The simplest boron hydride – diborane – is one of the most stable compounds of this class and is one of the least active in its attack on the grease in joints and taps. Until recently, most of the methods for its synthesis gave complex mixtures of volatile substances containing relatively little diborane, and its isolation from these mixtures was a very difficult task.

Stock, the pioneer in the systematic investigation of the boron hydrides, obtained diborane by prolonged fractionation of the hydrolysis products of so-called magnesium boride [1-4]. Later, Schlesinger and Burg [5] and Stock [6] obtained diborane by passing a mixture of boron halides and hydrogen through an electric discharge, but the yield did not exceed 6%. Hurd [7] prepared diborane by the reduction of boron halides with hydrogen in presence of metals and metal hydrides at high temperatures, and the product was again a difficultly separable mixture having a relatively low diborane content. In 1947 Schlesinger and coworkers [8] made use of the reaction of lithium aluminum hydride with boron trichloride for the preparation of diborane.

With the object of preparing diborane, at the end of 1949 we carried out a systematic study of the reduction of simple inorganic boron compounds with lithium hydride. For this purpose we used boron halides and sulfides, alkali-metal fluoborates, and other compounds. We found that, apart from boron trifluoride in ether solutions, all these substances react with lithium hydride with deflagration and the separation of elementary boron. After a considerable induction period lithium hydride reacted with a dilute ethereal solution of boron trifluoride at room temperature with separation of diborane; when the ether complex of boron trifluoride ("boron trifluoride etherate", a liquid, b.p. 126°) was used, reaction set in very quickly. The gas evolved was almost pure diborane, free from impurities apart from ether vapor. However, the reaction was found to be very capricious, giving yields that varied over the range 20-60%, and systematic work was necessary in order to ensure a reproducible yield.

Since we began this work some patents and papers have been published on the preparation of diborane by reaction between boron trifluoride and lithium hydride in an ether medium. Two patents were published in 1951 on the preparation of diborane by heating a mixture of lithium hydride and boron trifluoride in ether with simultaneous removal of diborane by distillation [9,10]. In a paper by Schapiro and coworkers in 1952 [11] a method is described for the preparation of diborane by reaction between boron trifluoride etherate and lithium aluminum hydride, and in a paper by Elliott, Boldebuck, and Roedel [12] its preparation by reaction of lithium hydride and boron trifluoride etherate is described. In this last investigation numerous experiments were carried out under various conditions, and the results were examined from the point of view of the possibility of the occurrence of two reactions:

$$6LiH + 2BF_3 \xrightarrow{\text{activator}} B_2H_6 + 6LiF$$

$$6LiH + 8BF_3 \rightarrow B_2H_6 + 6\,LiBF_4.$$

In presence of sufficient activator, the reaction proceeds in stages:

$$6LiH + 1.5BF_3 \xrightarrow{\text{activator}} 1.5LiBH_4 + 4.5LiF$$

$$1.5\ LiBH_4 + 0.5\ BF_3 \rightarrow B_2H_6 + 1.5\ LiF.$$

The authors point out the great complexity of the reaction and state that the presence of an ether-soluble activator ($LiBH_4$ or $LiBH(OCH_3)_3$) results in preferential conversion to $LiBH_4$, whereas in absence of an activator the reaction proceeds in the direction of the formation of B_2H_6 and $LiBF_4$. High pressures and the use of a tetrahydrofuran medium, in which diborane is highly soluble [13], favor the formation of lithium borohydride. The inconsistency of the yields is particularly emphasized in this paper. In a paper by Schlesinger and coworkers [14] it is stated that boron trifluoride etherate reacts with lithium hydride according to Equation 1 at a rate that depends on the degree of grinding of the lithium hydride, and the maximum yields that they give are not greater than 40-60% with respect to boron. The following intermediate stages are indicated in this paper:

$$3\ LiH + 3\ BF_3 \cdot O(C_2H_5)_2 \rightarrow 3\ LiBHF_3 + 3\ (C_2H_5)_2O;$$

$$3\ LiBHF_3 + BF_3 \cdot (C_2H_5)_2O \rightarrow \frac{1}{2}\ B_2H_6 + 3\ LiBF_4 + (C_2H_5)_2O.$$

It is pointed out that successive additions of the etherate react progressively less vigorously, in spite of the presence of excess of lithium hydride in the reaction mixture. The authors regard this reaction as difficult and non-quantitative, and they prefer the reaction of boron trifluoride with $NaBH(OCH_3)_3$, which gives more consistent yields of diborane. In all the published investigations, therefore, references are made to the complexity of the reaction and the inconsistency of the yields of diborane. For this reason we considered it desirable to publish our results on the reaction of boron trifluoride with lithium hydride, which were verified in numerous experiments under laboratory conditions.

EXPERIMENTAL

Original Substances. Lithium hydride LiH was the commercial quality, a fused crystalline mass containing 90-98% of LiH. It was ground as finely as possible in a mortar, sieved, and used immediately in the reaction. The use of hydride powder that has been kept for a long time results in a long period of induction with subsequent violent reaction.

Boron trifluoride BF_3 was prepared by reaction of boric anhydride with potassium fluoborate and concentrated sulfuric acid [15]. In order to remove hydrogen fluoride and water vapor impurities, the gas was passed through a trap containing concentrated sulfuric acid saturated with boric anhydride in the cold.

Boron trifluoride etherate $BF_3 \cdot (C_2H_5)_2O$ was prepared by saturating absolute ether with boron trifluoride and then distilling at atmospheric pressure; b.p. 126°. When kept, the etherate darkens in color; freshly distilled material must be used in the reaction.

Diethyl ether was first dried with calcined calcium chloride and then distilled and kept over sodium for a long time.

Investigation of Solid Reaction Products. After the reaction, during which gaseous diborane was removed, and removal of ether, a white solid remained in the reaction vessel. In order to determine the exact yield of the reaction with respect to the reactants consumed, it was necessary to determine the composition of this solid.

A test for $LiBH_4$ was carried out by adding 3-4 drops of water or dilute acid to a small amount of an ether extract of the solid. The presence of $LiBH_4$ was indicated by vigorous evolution of hydrogen. Lithium borohydride was isolated quantitatively from the solid by repeated washing with ether on a glass funnel with a porous bottom, filtration under a pressure of dry nitrogen, removal of ether from the filtrate under atmospheric pressure, and drying of the product in a vacuum at 90-100°. The active-hydrogen content of the lithium borohydride was determined by decomposing a sample with a weakly acid solution of a nickel salt [16].

In order to test for the presence of $LiBF_4$, an aqueous solution of a little of the solid was neutralized to methyl orange with hydrochloric acid and mixed with concentrated calcium chloride solution. In presence of $LiBF_4$ the reaction

$$LiBF_4 + 2CaCl_2 + 3H_2O \rightarrow H_3BO_3 + LiCl + 3HCl + 2CaF_2.$$

occurred; there was an indicator change to pink, which became bright red with simultaneous precipitation of CaF_2, when the solution was heated.

For the quantitative determination of $LiBF_4$, a sample of the solid weighing 0.2-0.3 g was dissolved in the least possible amount of water, the solution was neutralized to methyl orange, a strong neutral solution of calcium chloride was added, and the solution was brought almost to the boil, at which it was maintained for 10-15 minutes. The hot solution was titrated with 0.1 N NaOH until almost neutral, and it was then again heated almost to the boil and again titrated. Heating and titration were continued until 1-2 ml of alkali was required for neutralization. The solution was then boiled again for 30 minutes, cooled to room temperature, and titrated for the last time. At this point the hydrolysis of the BF_4^- ion would be practically complete [17]. The calculation of the lithium fluoborate concentration was carried out on the basis of the above equation.

Determination of unchanged lithium hydride in the solid was carried out after removal of lithium borohydride by ether extraction and removal of ether under vacuum. A sample weighing 0.02-0.03 g was decomposed with water, and the hydrogen evolved was collected in a gas buret. The volume was adjusted to normal conditions, and the LiH content of the solid was calculated.

Determination of boron was carried out on the solution after determining the BF_4^- ion and filtering off the precipitate of potassium fluoride. The solution was made up to 250 ml in a measuring flask. An aliquot of this was neutralized to methyl red, mannitol was added, and the solution was titrated to phenolphthalein with 0.1 N NaOH.

For the determination of total fluorine, the precipitate of CaF_2 remaining after the determination of fluorine bound in the form of $LiBF_4$ was filtered off, carefully washed with water, and placed together with the filter paper in a platinum crucible. After being dried and then ignited at 500-600°, the precipitate was weighed. A simple calculation gave the fluorine content.

Lithium was determined gravimetrically in the form of Li_2SO_4, boron being first removed in the form of trimethyl borate and fluorine by repeated evaporation to dryness with sulfuric acid and methanol, the latter being added periodically.

Experiments with Stoichiometric Proportions and with Excess of One or Other Reactant. In the first series of experiments on the preparation of diborane (Table 1), the reaction vessel was a three-necked flask fitted with mercury-sealed mechanical stirrer, dropping funnel, an arrangement for scattering the lithium hydride, and a very efficient reflux condenser, the free end of which was connected to traps cooled with solid carbon dioxide for trapping ether vapor. The yield of diborane in these experiments was determined by absorbing the gas evolved in 20-30% caustic potash solution, acidifying the solution, and determining the boric acid content [18,19], from which the yield of diborane was calculated. In the experiments in which diborane was actually isolated, for the complete removal of ether vapor it was first passed through traps containing concentrated sulfuric acid and then through traps cooled with a mixture of solid carbon dioxide and acetone; it was collected in receivers cooled with liquid nitrogen. In these experiments air was first displaced from the apparatus with dry hydrogen.

In some experiments lithium hydride powder was added to boron trifluoride etherate (Experiments 1 and 3). In most of the experiments, after displacement of air with dry hydrogen or nitrogen, the whole of the amount of finely ground lithium hydride required for the reaction was placed in the reactor and made into a suspension with the minimum amount of ether, and 25-30% of the amount of etherate necessary for reaction in accordance with Equation 1 was added rapidly. The temperature of the mixture then rose to 40°, the mixture boiled, and evolution of diborane set in immediately. The remainder of the etherate was then added gradually. The diborane formed was carried away by a current of dry hydrogen or nitrogen.

An examination of Table 1, which gives the conditions and results of experiments with stoichiometric proportions of reactants (Equation 1), with excess of lithium hydride, and with excess of boron trifluoride, reveals certain regularities. Considerable dilution of the boron trifluoride etherate with ether (Experiment 1) delays the start of the reaction, whereas the addition of small amounts of ether to the lithium hydride at the beginning and in the course of the reaction facilitates mixing and the evolution of diborane. The best yields of diborane with respect to boron are attained with an excess of lithium hydride of 25% and more. The use of a considerable excess of the etherate lowers the yield of diborane with respect to boron to 20% (Experiment 13); moreover, in spite of the excess of etherate, much of the lithium hydride (as much as 50% or higher) does not react. The probable cause of this is the envelopment of hydride particles by solid reaction products – first lithium fluoride, and then lithium fluoborate – which make the particles incapable of further reaction with

TABLE 1

Experiments on the Preparation of Diborane using Various Relative Amounts of $BF_3 \cdot (C_2H_5)_2O$ and LiH

Experiment No.	Amount taken (g) of LiH	Amount taken (g) of BF_3	$\frac{BF_3}{LiH}$	Yield of B_2H_6 (%) Based on BF_3 (Equation 1)	Yield of B_2H_6 (%) Based on LiH	Yield of $LiBH_4$ (% on BF_3 taken)	Yield of $LiBF_4$ (% on BF_3 taken)	Procedure
1	4.2	21.8	1 : 3.5	49	43.5	Not determined	Not determined	Etherate highly diluted with ether. Long induction period. Hydride added to BF_3 etherate.
2	4.55	12.7	1 : 6.3	53	40	30.7	"	Etherate diluted with 25 ml of ether. All hydride added at once.
3	2.4	14.0	1 : 3	19.7	23.79	Nil	"	Hydride added to undiluted BF_3 etherate
4	5.1	28.36	1 : 3.2	25	22.6	3.83	"	Ditto
5	2.7	11.22	1 : 4.2	43.4	30.5	Nil	"	Gradual addition of hydride to etherate. Mixture stood 24 hours During reaction 20 ml of ether added.
6	3.2	18.7	1 : 3	28.9	27.7	"	"	Ditto
7	7.5	42.6	1 : 3.1	39.1	33	"	"	Hydride gradually sprinkled into etherate; mixture warmed periodically.
8	22	118	1 : 3.3	46.5	42.2	"	"	Etherate added in two portions; hydride added gradually.
9	13	71	1 : 3.2	44.4	41.1	"	40	Ditto
10	12	71	1 : 3	42.9	42.9	"	44.6	Alternating gradual additions of etherate and hydride.
11	10	42.6	1 : 4.1	58.72	42.30	Not determined	Not determined	Ditto
12	7.5	42.6	1 : 3	47.53	47.53	"	"	Etherate gradually added dropwise to suspension of LiH in 30 ml of ether.
13	2.7	28.24	1 : 1.7	22.46	30.5	Nil	61.24	Ditto
14	1.2	28.24	4 : 3	23.02	62.1	"	46.13	Ditto
15	5.0	14.12	1 : 6	Not determined		15.2	Not determined	Reaction at 0°; etherate gradually added to suspension of hydride in 10 ml of ether.
16	6.7	28.4	1 : 4.1	63	45.0	22.7	Traces	Etherate slowly added to suspension of hydride in 60 ml of ether at 15°

the etherate. For the best utilization of the boron, therefore, it is necessary to take excess of lithium hydride over the amount required according to Equation 1.

Experiments on the preparation of diborane from reaction mixtures containing small additions of lithium borohydride, lithium aluminum hydride, sodium hydride, or trimethyl borate showed that lithium borohydride and trimethyl borate are highly active, particularly the former. The addition of lithium borohydride, even in small amounts, causes the initiation of the reaction and practically eliminates the induction period.

The effect of temperature can be derived from comparisons between various experiments. For example, in 2 reaction was between 12.7 g (0.09 mole) of $BF_3 \cdot (C_2H_5)_2O$ and 4.55 g (0.57 mole) of LiH (BF_3 : LiH = 1 : 6) at 18°, and 2.6 g of lithium borohydride etherate was isolated. When reaction between the same amounts of reactants was carried out at the boiling point of ether, $LiBH_4$ was completely absent from the ether layer. At 0° (Exp. 15) formation of diborane was at a minimum and reaction proceeded preferentially in the direction of $LiBH_4$ formation.

Comparison between Experiments 4 and 5 shows the effect of the order of addition of reactants: alternation of the addition of etherate and hydride improves the yield of diborane, but gradual addition of etherate to the whole amount of the hydride as a suspension in ether (Experiment 16) gives the best yields of diborane.

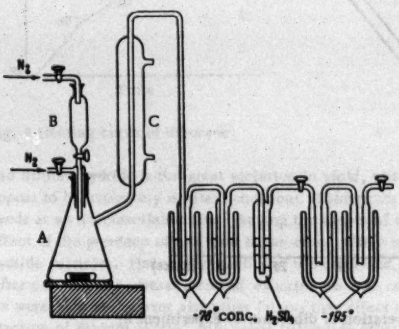

Fig. 1. Laboratory apparatus for the preparation of diborane.

Experiments with Excess of Boron Trifluoride Etherate.* The next series of experiments, for which reaction balance sheets were calculated, was based on an analysis of the results of the first series (Table 1) with the object of improving the yield of diborane, both with respect to boron and with respect to lithium hydride. The yield calculated on the amount of lithium hydride taken is very important, for excess of hydride in the solid reaction product is difficult to utilize or recover, whereas unchanged boron trifluoride can be recovered by distillation during the course of the calcination of the precipitate. In this series of experiments the apparatus used consisted of a reactor A containing a magnetic stirrer (Fig. 1) and fitted with a dropping funnel B, a tube with a tap for introduction of nitrogen, and a reflux condenser C attached to traps. A suspension of the whole of the lithium hydride in a little ether was prepared in the reactor, and 15-25% of the total amount of etherate was added rapidly. A uniform stream of liberated diborane was then maintained by the addition of fresh portions of etherate. In these experiments the diborane was absorbed in dry pyridine, with which it formed the complex $C_5H_5N \cdot BH_3$ [20]. The active hydrogen in the pyridine solution was subsequently determined.

Table 2 gives the amounts of the reactants and products for some experiments of this series. For Experiments 3 and 4 curves showing the time-dependence of the liberation of diborane are given (Fig. 2). In order to indicate the procedure, we describe one of these experiments below. In most of the experiments, not only the gaseous, but also the solid reaction products were investigated, so that the actual equation of the reaction could be given (last column of Table 2).

These equations were obtained by multiplying the numbers of moles of lithium hydride and boron trifluoride etherate brought into reaction by a factor that brings the number of moles of lithium hydride to six, so that a comparison can be made with Equation 1. As lithium borohydride was not found in any of the experiments and the lithium hydride was utilized almost quantitatively, we regarded the yield of diborane as almost quantitative. This is in satisfactory agreement with results on the determination of the yield of diborane when correction is made for unavoidable leakage; Experiment 1 is exceptional, since a considerable loss of the diborane occurred.

Description of Experiment 4 (Table 2). Boron trifluoride etherate (21.3 g) was added rapidly to an electromagnetically stirred suspension of 6.4 g (0.8 mole) of lithium hydride in 15 ml of absolute ether. The remainder of the etherate was added gradually in such a way that uniform liberation of diborane was maintained.

* Excess of etherate is to be understood as referring to the stoichiometry of Equation 1.

In all, 42.3 g (0.30 mole) of etherate was added. Further addition of etherate did not result in liberation of more diborane. As necessary, more ether was added to the reaction mixture (three 15-ml portions). The diborane evolved was absorbed with dry pyridine. The pyridine traps were changed periodically so that the course of the liberation of diborane could be followed (Fig. 2). The yield of diborane with respect to boron trifluoride etherate (according to Equation 1) was 83.4%, and with respect to lithium hydride it was 94.6%. Other experiments of this series were carried out in a similar way. By this procedure, therefore, all the lithium hydride can be caused to react without an appreciable reduction in the yield of diborane calculated on a boron basis.

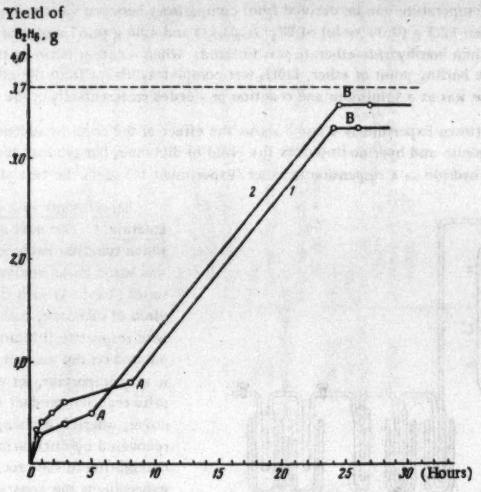

Fig. 2. Time-dependence of liberation of diborane: 1) Experiment 3; 2) Experiment 4.

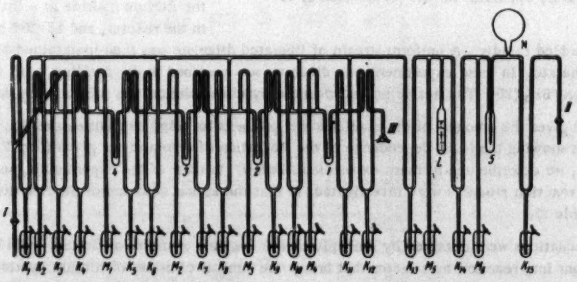

Fig. 3. Diagram of vacuum apparatus for the refining of diborane and the determination of its constants.

Determination of the Purity of the Diborane. The diborane obtained by the reaction investigated contains only ether vapor as impurity. The solutions obtained by absorption of the diborane in traps containing water gave no reaction for fluorine with saturated calcium chloride solution. Passage of the diborane through traps containing

concentrated sulfuric acid and traps cooled with a mixture of solid carbon dioxide and acetone (-78°) freed it from ether vapor. In order to establish the purity of the diborane, it was fractionated by the fractional-condensation method and the physical constants of the fractions were determined, this being carried out in a special vacuum apparatus (Fig. 3) constructed in accordance with Stock's recommendations [4], in which the diborane came into contact only with glass and mercury. The fractionation showed that the gas consisted of one fraction only, this being collected at -170° in the form of a white crystalline mass.

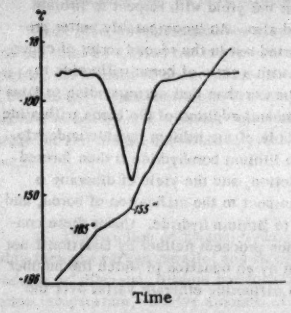

Fig. 4 Heating curve of diborane.

The substance was characterized by vapor-pressure and melting-point determinations. The vapor pressure, which was determined by Stock's method [4] using a gas thermometer (filled with ethylene), was found to be 166.5 mm at -119° (m.p. of diethyl ether), whereas Stock obtained a value of 167.5-168 mm for the same temperature. Heating curves for samples of diborane in the range from -195° to -100° (Fig. 4) have only one halt, corresponding to the endothermic process of fusion; the start of this was at -165°, both for "crude", and also for carefully fractionated diborane (Stock obtained -165.5°). The diborane obtained by the method described was therefore almost completely pure.

DISCUSSION OF RESULTS

An unsatisfactory feature of the preparation of diborane by reaction between boron trifluoride etherate and lithium hydride is the great variation in yield, which varies from 20% to 90% with respect to boron under what appear to be extremely similar conditions. Sometimes the reaction has a long period of induction and then proceeds at an uncontrollable rate. Among the causes of this great variation in yield there is, in the first place, the effect of the presence of moisture in the ether, which results in the formation of films of oxide on the lithium hydride particles. Hence, the quality of the ether and lithium hydride is subject to very exacting requirements. After carrying out several series of experiments with complete analysis of the gaseous, liquid, and solid phases, we were able to discover also other factors that affect the yield of diborane. Our investigation showed that the reaction of lithium hydride with boron trifluoride etherate cannot be described by any one equation, but consists in a series of parallel reactions having successive stages.

Apart from the reactions described by Equations 1 and 2, if the intermediate stages are not counted, the following reactions are also possible:

$$4\,LiH + BF_3 \cdot (C_2H_5)_2O \rightarrow LiBH_4 + 3\,LiF. \quad (3)$$

$$BF_3 + LiF = LiBF_4. \quad (4)$$

$$BF_3 + 3\,LiBH_4 = B_2H_6 + 3\,LiF. \quad (5)$$

The transformation of boron trifluoride goes in three directions: formation of diborane, of lithium borohydride, and of lithium fluoborate. Taking into account the solubilities of the compounds obtained in ether [12] (B_2H_6 - 1.1 g/100 g; $LiBF_4$ - 1.9 g/100 g; $LiBH_4$ - 3.0 g/100 g; LiF - 0.05 g/100 g) and our experiments showing that only diborane is present in the gas phase, we may suppose that the solid phase remaining after distillation of ether may contain, apart from unchanged lithium hydride, lithium fluoride and the boron-containing compounds lithium fluoborate and lithium borohydride. Depending on temperature, dilution with ether, proportions of reactants, and the order of their addition, the reaction may proceed in the direction of a higher or lower relative yield of diborane.

When reaction is brought about at room temperature with an excess of lithium hydride, the temperature of

TABLE 2
Experiments with Excess of Boron Trifluoride Etherate

Experiment No.	Amount taken (g) of $BF_3 \cdot (C_2H_5)_2O$	Amount taken (g) of LiH	BF_3 / LiH	Yield of diborane (%) with respect to boron	Yield of diborane (%) with respect to hydride	Yield (% on BF_3) of $LiBH_4$	Yield (% on BF_3) of $LiBF_4$	Equation of reaction
1	46.15 (0.325)	6.4 (0.8)	1 : 2.45	53.1	65.3	Nil	18.0	$6LiH + 2.44BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 0.44LiBF_4 + 5.56LiF + 2.44(C_2H_5)_2O$
2	49.7 (0.35)	5.4 (0.675)	1 : 2	60.82	96.34	Nil	37.5	$6LiH + 3.2BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 4.8LiF + 1.2LiBF_4 + 3.2(C_2H_5)_2O$
3	60.3 (0.425)	6.4 (0.8)	1 : 2	57.0	88.1	Nil	37.5	Dimer
4	42.3 (0.30)	6.4 (0.8)	1 : 2.7	83.45	94.6	Nil	11.1	$6LiH + 2.25BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 5.75LiF + 0.25LiBF_4 + 2.25 \cdot (C_2H_5)_2O$

of the mixture rises to 25-35° and there is preferential formation of diborane; under these conditions lithium borohydride does not accumulate in the ether solution. However, much of the boron remains in the precipitate in the form of $LiBF_4$ and the lithium hydride is not utilized fully. When there is a considerable excess of lithium trifluoride, not only is the yield with respect to boron lowered, but the yield with respect to lithium hydride is lowered also. An incomparably better procedure is that carried out in the second series of experiments (Table 2) with a ratio of boron trifluoride to lithium hydride greater than that corresponding to Equation 1 and with gradual addition of the boron trifluoride etherate to the whole of the lithium hydride under vigorous stirring. No lithium borohydride is then formed in the overall reaction, and the yield of diborane is raised both with respect to the utilization of boron, and also with respect to lithium hydride. Under these conditions, the reaction proceeds neither by Equation 1 nor by Equation 2, but by an equation in which the number of moles of boron trifluoride etherate varies over the range 2.25-2.8.

The curve for the time-dependence of the liberation of diborane has a well defined point of inflection A (Fig. 2). This shows that, with gradual addition of etherate, the reaction proceeds in two stages. In the first stage, in which there is a large excess of lithium hydride, the comparatively slow liberation of diborane is associated with the accumulation of active intermediate reaction products – possibly also lithium borohydride – without appreciable formation of lithium fluoborate. The second stage consists in the reaction of fresh portions of etherate with the remaining lithium hydride and with the accumulated active intermediaries, including lithium borohydride. Most of the diborane is obtained at this stage, and there is a corresponding sharp rise in the curve for the liberation of diborane (Fig. 2).

At both stages the reaction probably has a multistage mechanism with formation of the intermediaries $LiHBF_3$, $LiBH_2F_2$, and $LiBH_3F$. The last two compounds may give diborane, since their molecules contain a "ready-made" borine group BH_3:

$$2\,LiBH_3F \rightarrow B_2H_6 + 2\,LiF$$

or

$$2LiBH_3F + 2BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 2LiBF_4,$$
$$3\,LiBH_4 + BF_3 \cdot (C_2H_5)_2O \rightarrow 2\,B_2H_6 + 3\,LiF.$$

Simultaneously, particularly in the first stage, a reaction occurs between diborane and excess of lithium hydride:

$$2\,LiH + B_2H_6 \rightarrow 2\,LiBH_4$$

and there is also the reaction (4) in the case of excess

of boron trifluoride. Moreoever, in the initial stage of the reaction, while the temperature of the reaction mixture is rising to 40°, disproportionation reactions are possible for the intermediate reduction products:

$$2\ LiHBF_3 \rightarrow LiBH_2F_2 + LiBF_4;$$

$$3\ LiBH_2F_2 \rightarrow B_2H_6 + LiBF_4 + 2\ LiF;$$

$$4\ LiBHF_3 \rightarrow LiBH_4 + 3\ LiBF_4 \text{ etc.}$$

The reactions that we have cited here give some idea of the complexity of the process studied.

From these considerations we may conclude that, for maximum yields of diborane, the initial stage of the reaction must be carried out in presence of excess of lithium hydride, and that, for the best utilization of the hydride, the amount of boron trifluoride etherate taken must be greater than that corresponding to the stoichiometry of Equation 1. These conditions are attained by the procedure used in Experiment 4 (Table 2). Carrying out the reaction in accordance with our description of this experiment ensures the preparation of highly pure diborane in consistent and almost quantitative yield with respect to lithium hydride and to the boron trifluoride etherate that reacts.

SUMMARY

1. The reaction of lithium hydride with boron trifluoride etherate has a complex mechanism, which probably includes various parallel and successive reactions leading to the formation, as the ultimate boron-containing products, of diborane, lithium borohydride, and lithium fluoborate. The yield of diborane is dependent on reaction temperature, relative amounts of reactants, degree of agitation of the reaction mixture, and order of addition of reactants.

2. An almost quantitative yield with respect to both reactants is attained by carrying out the reaction at somewhat raised temperature (25-30°) in the initial stage, at a BF_3 : LiH ratio of 1 : 2.4-2.8, and with gradual addition under constant stirring of lithium trifluoride etherate to lithium hydride.

3. The reaction studied is the simplest and most economical method for the preparation of highly pure diborane under laboratory conditions, and it opens up wide possibilities for the further study of the chemistry of boron hydrides and their derivatives.

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MECHANISM OF THE DEACTIVATION OF NICKEL CATALYSTS BY STEAM UNDER PRESSURE

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Water is one of the most frequently encountered impurities in catalytic reduction and hydrogenation processes; it is formed by the reduction of metal oxides and oxygen-containing organic compounds. Water is a reaction component in transformations of hydrocarbons and carbon monoxide; it is used as a solvent and diluent. However, the effect of water vapor on nickel hydrogenation catalysts has been inadequately investigated.

Tsutsumi and coworkers [1] noted that small amounts of water greatly reduce the activity of a nickel catalyst in fat-hydrogenation reactions. Slovokhotova and Ivanov [2] found that the rate of dehydrogenation of cyclohexane at 250-300° over a nickel-alumina catalyst was reduced by a factor of five in presence of water vapor. Arnold and Atwood [3] state that nickel deposited on a complex mixture of oxides is of low stability as a catalyst for the transformation of hydrocarbons by means of steam.

In an investigation of the properties of nickel catalysts prepared by reduction with hydrogen at a pressure of 500 atm, we concluded that the cause of their low activity was the presence of water vapor in the sphere of the reduction reaction. In this connection we studied the effect of water vapor purposely introduced into the reduction zone in the treatment of nickelous oxide with hydrogen under pressure. It was found that steam under pressure brings about a far-reaching irreversible change in the catalyst components, namely their recrystallization. Our results make it possible to approach the question of the mechanism of the deactivation of of metal catalysts with water vapor from a new viewpoint.

EXPERIMENTAL

Experimental Procedure

The catalysts were prepared by coprecipitation from a mixture of molar nitrate solutions with 30% sodium hydroxide. The product was decomposed to give a mixture of oxides corresponding to 35% NiO and 65% Al_2O_3 (or 65% MgO).

The reduced catalyst or carrier-supported nickelous oxide was placed in a stainless-steel beaker and treated for five hours at 350° with a mixture of steam (100 atm) and hydrogen (700 atm) in a special high-pressure reactor. The treated mass was removed from the cooled reactor and reduced with electrolytic hydrogen at 350° and normal pressure. The activity of the catalyst was characterized by the degree of hydrogenation of benzene (at 120° and at a space velocity of 0.3 $hour^{-1}$) or the degree of dehydrogenation of cyclohexane (at 300° and at a space velocity of 0.3 $hour^{-1}$), determined in continuous-flow apparatus. The degree of hydrogenation of benzene and the degree of dehydrogenation of cyclohexane were determined refractometrically [4].

Effect of a Mixture of Steam and Hydrogen under Pressure on the Activity of a Nickel-Alumina Catalyst

Experiments 1 and 2 were carried out with commercial nickel-alumina catalyst containing 50% of nickel. Over this catalyst benzene was hydrogenated to the extent of 97% at 120°. It will be seen from Table 1 that, after the steam-hydrogen treatment, the degree of hydrogenation of benzene was only 14.4%. The catalyst was then reduced with hydrogen for five hours at 350° and normal pressure. Its activity then increased

considerably: the degree of hydrogenation of benzene was 56.2%. After a further reduction with hydrogen for six hours under the same conditions, the activity of the catalyst was almost completely recovered. It is thus possible to regenerate a reduced catalyst that has been deactivated by treatment with steam. However, the deactivated catalyst must be treated with hydrogen for a fairly long time.

TABLE 1

Effect of Treatment with a Steam-Hydrogen Mixture Under Pressure on the Activity of a Nickel-Alumina Catalyst. Conditions of treatment: hydrogen pressure 700 atm; steam pressure 100 atm; duration five hours; temperature 350°

Expt. No.	Sample of $Ni\text{-}Al_2O_3$	Duration of reduction with hydrogen * (hours)	Degree of hydrogenation of benzene (%)
1	Untreated	6	97.4
2	Treated	–	14.4
		5	56.2
		6	94.0

* At 350° under normal pressure.

Effect of Treatment of Carrier-supported Nickelous Oxide with a Mixture of steam and Hydrogen under Pressure

Nickelous oxide on a carrier was treated for five hours at 350° with a mixture of steam and hydrogen. It will be seen from Table 2 that sample No. 7 of nickelous oxide on alumina, treated in this way and then reduced with hydrogen for five hours at 350° and normal pressure, was almost completely inactive as a catalyst: the degree of hydrogenation of benzene at 120° was only 6.4%. After further reduction with hydrogen for eight hours, the activity of the catalyst did not increase. After a third reduction with hydrogen for eight hours, the activity of the catalyst was still low: the degree of hydrogenation of benzene at 180° was 9.5% (Experiment 4). For a catalyst prepared from the same sample without treatment with steam, the degree of hydrogenation of benzene was 91.6% and the degree of dehydrogenation of cyclohexane was 63% (Experiment 3).

Similar results were obtained with sample No. 8. The catalyst prepared from this sample and not subjected to the action of steam was very active: the degree of hydrogenation of benzene was 98.8%, and the degree of dehydrogenation of cyclohexane was 78.8%. The sample was treated with a mixture of steam and hydrogen under pressure at 350°, and subsequent reduction with hydrogen at atmospheric pressure at 350° gave an inactive catalyst: the degree of hydrogenation of benzene at 120° was 1.2%. After further reduction with hydrogen at ordinary pressure and 350° for eight hours and then at 425° for five hours, it remained almost inactive (Experiments 5 and 6).

Similar results were obtained when the catalyst was prepared from nickelous oxide and magnesia, subsequently treated with a mixture of steam and hydrogen under pressure. Reduction with hydrogen for five hours at 350° and ordinary pressure gave an inactive catalyst: the degree of hydrogenation of benzene was 0.2% at 120° and 8.8% at 180°. After further reduction with hydrogen for eight hours under similar conditions, the degree of hydrogenation of benzene attained 19%. The catalyst prepared from the same sample of nickelous oxide on magnesia, but not subjected to the action of steam, hydrogenated benzene to the extent of 91.6% and dehydrogenated cyclohexane to the extent of 46.4% (Experiments 7 and 8).

The results obtained with three samples of nickelous oxide on alumina or magnesia show that, when reduced with hydrogen in presence of steam, carrier-supported nickelous oxide suffers an irreversible change. An active catalyst was not obtained from the nickelous oxide even after reduction with hydrogen for 13-21 hours at 350° and ordinary pressure.

Similar results were obtained when nickelous oxides on carriers were treated with a mixture of steam and nitrogen under pressure. However, they were somewhat more active than samples treated with a mixture of steam and hydrogen (Experiments 9 and 10) (Table 3).

Effect of Treatment of Alumina-supported Nickelous Oxide with Steam

In order to determine the effect of treating nickelous oxide with steam in absence of hydrogen or nitrogen, a series of experiments was carried out in which the following procedure was adopted. Nickelous oxide on alumina was heated in an autoclave with a definite volume of distilled water. The temperature was measured with a thermocouple placed in the pocket of the autoclave. At the end of the experiment, the contents were unloaded, dried at 100°, formed into shape, and reduced with hydrogen at 350°. The activity of the catalyst was then tested for the hydrogenation of benzene or the dehydrogenation of cyclohexane by the usual method.

TABLE 2

Effect of Treatment of Carrier-supported Nickelous Oxide with a Mixture of Steam and Hydrogen under Pressure*. Conditions of treatment: hydrogen pressure 700 atm; steam pressure 100 atm; duration five hours; temperature 350°

Experiment No.	Sample: composition	Sample: treatment	Duration of reduction with hydrogen (hours)**	Temperature (°C)	Degree of hydrogenation of benzene (%)
3	$NiO—Al_2O_3$ № 7	Untreated	3	120	91.6
4		Treated	5	120	6.4
			13	120	6.0
			21	180	9.5
5	$NiO—Al_2O_3$ № 8	Untreated	1.5	120	98.8
6		Treated	5	120	1.2
			13	180	0.8
			18***	180	1.2
7***	NiO—MgO № 2	Untreated	10	120	91.6
8		Treated	5	120	0.2
			—	180	8.8
			13	180	19.0

* The catalysts prepared from the untreated samples dehydrogenated cyclohexane at 300° to the following extents: No. 7,63%; No. 8,78.8%; No. 2,46.4%.

** At 350° under normal pressure.

*** The last five hours of the reduction were at 425°.

TABLE 3

Effect of Treatment of Carrier-supported Nickelous Oxide with a Mixture of Steam and Nitrogen under Pressure . Conditions of treatment: nitrogen pressure 700 atm; steam pressure 100 atm; duration five hours; temperature 350°.

Experiment No.	Sample: composition	Sample: treatment	Duration of reaction with hydrogen (hours)*	Temperature (°C)	Degree of hydrogenation of benzene (%)
3	$NiO—Al_2O_3$ № 7	Untreated	3	120	91.6
9		Treated	5	120	20.8
7	NiO—MgO № 2	Untreated	10	120	91.6
10		Treated	5	120	1.2
			13	180	50.0
			21	180	59.0

* At 350° under normal pressure.

It will be seen from Table 4 (Experiment 11) that nickelous oxide on alumina, treated for five hours at 350° with steam under a pressure of 100 atm and then reduced with hydrogen, becomes quite inert as a catalyst. A

similar result was obtained with the same sample of nickelous oxide on alumina treated with steam for two hours (Experiment 12). The two catalysts from Experiments 11 and 12 were then mixed and further reduced with hydrogen for 20 hours at 350° at normal pressure, the total duration of the hydrogen treatment then being 25-33 hours. Even then, however, the catalyst was found to be quite inactive (Experiment 13). It follows from Experiment 14 that, when the temperature of the steam treatment of nickelous oxide on alumina in the autoclave was lowered to 300°, a catalyst was obtained which was again of low activity: the degree of hydrogenation of benzene in its presence was 3.4%. In Experiment 15 no water was added. It was found that even the very small amount of water vapor that is liberated during dehydration at 350° is sufficient to reduce the activity of the catalyst appreciably (Table 4).

TABLE 4

Effect of the Treatment of Alumia-supported Nickelous Oxide (Sample No. 8) with Steam under Pressure. Conditions of treatment: steam pressure 100 atm; duration five hours; temperature 350°.

Experiment No.	Duration of reduction with hydrogen (hours)*	Degree of hydrogenation of benzene (%)	Degree of dehydrogenation of cyclohexane (%)
5	1.5	98.8	78.8
11	5	0.3	—
12**	5	0.3	—
	13	0.2	0.0
13	25—33	0.2	—
14***	5	3.4	10.6
	13	0.2	—
15****	5	71.2	40.8

* At 350° and normal pressure.
** Duration of steam treatment two hours.
*** Treated with steam at 300°
**** No water was added.

The results given in Table 2 and 4 show that a catalyst prepared from carrier-supported nickelous oxide treated with steam is just as inactive as a nickelous oxide preparation treated with a mixture of steam and hydrogen.

Effect of Treatment of Nickelous Oxide Alone with Steam

The above-described results refer to nickelous oxide supported on a carrier. It was essential to determine the effect of steam treatment of nickelous oxide alone, in absence of carrier. With this object, nickelous oxide prepared by precipitation of a molar solution of the nitrate with sodium hydroxide was taken in an amount of 4.2 g (10 ml) and reduced with hydrogen for ten hours at 350°. Another portion of the same sample of nickelous oxide was pretreated for five hours at 350° with steam at 180 atm, and some of the product (4.2 g, i.e., 2.5 ml) was reduced for ten hours at 350°. Activity tests showed that, with the catalyst prepared from nickelous oxide not treated with steam, benzene was hydrogenated to the extent of 93.4%, and cyclohexane was dehydrogenated to the extent of 37.8%. The activity of the catalyst prepared from the steam-treated nickelous oxide was considerably lower: degree of hydrogenation of benzene 52-60% and degree of dehydrogenation of cyclohexane 20-21%. As will be seen, the effect of steam under given conditions on nickelous oxide without carrier is much less than on nickelous oxide supported by a carrier. This shows the very close association between the nickelous oxide and the carrier in the coprecipitated mixture.

Effect of Steam on the Activity of Nickel Catalysts

Investigations were made also on the effect of steam treatment on the activities of Raney nickel and of a catalyst prepared by the reduction of nickelous oxide.

a) Effect on the Activity of Nickel Prepared by the Reduction of Nickelous Oxide. A catalyst prepared by the reduction of 4.2 g (10 ml) of nickelous oxide with hydrogen (ten hours at 350°) was treated for five hours at 350° with steam at atmospheric pressure. The space velocity of passage of water was 0.5-0.6 hour^{-1}, and the total amount of water passed was 30 ml. After steam treatment, the catalyst was reduced with hydrogen for five hours at 350°. There was little change in activity: before steam treatment the degree of hydrogenation of benzene was 93.8%; after steam treatment it was 87.6%. It will be seen that treatment of reduced nickel with steam at ordinary pressure has only a slight effect on catalytic activity.

b) Effect on the Activity of Raney Nickel Catalyst. Samples of catalyst were prepared by leaching 50% nickel-aluminum alloy with 20% caustic alkali at 100°. The activity of the catalyst before and after steam treatment was characterized by the rate of hydrogenation of 0.25 g of phenyl vinyl ether in alcohol at 20°. A paste of the catalyst (10 g) was placed in a glass tube filled with nitrogen. The tube was heated in an electric furnace

TABLE 5

Deactivation of Raney Nickel Catalyst (10 g) with Steam at Atmospheric Pressure

Experiment No.	Conditions of steam treatment*		Amounts of hydrogen adsorbed in the first four minutes in the hydrogenation of 0.25 g of phenyl vinyl ether at 20° (ml/min)**
	Temperature (°C)	Duration (hours)	
16	Untreated		28.4—14.8—1.9—0.5
17	150	2	27.1—14.2—2.2—0.4
18	200	2	25.6—17.3—1.2—0.4
19	250	2	19.3—17.7—6.8—0.4
20	300	2	16.5—15.8—9.7—2.5

* 12 ml of water passed.

** 1 g of catalyst.

provided with a thermoregulator. During the warming-up period and throughout the experiment, a slow stream of oxygen-free nitrogen was passed through the tube. Water was admitted to the tube at a uniform space velocity of 0.6 hour^{-1}. The steam-treated catalyst was cooled in a stream of nitrogen and emptied out into water. It will be seen from Table 5 that treatment of the catalyst with steam for two hours at 150-200° did not lower the activity. Only steam treatment at 250-300° lowered the activity of the catalyst to an appreciable extent. Our results are in conflict with Aubry's assumption [5] concerning the interaction of Raney nickel and water at room temperature.

c) Effect of Treatment of Raney Nickel Catalyst with Steam at High Pressure. The catalyst was placed together with a definite volume of water in a 200-ml autoclave. The autoclave was hermetically sealed, blown out three times with nitrogen, and heated to the temperature of the experiment. At the end of the experiment the autoclave was cooled to room temperature. It was then opened rapidly, and water was poured over the catalyst. It will be seen from Table 6 that, when 10 g of catalyst was heated under pressure with 6-12 ml of water at only 150°, its activity was reduced by a factor of 3-4. Even the small amount of water contained in the moist Raney nickel paste was sufficient to deactivate the catalyst at 150° (Experiments 25 and 26). It is interesting to note that heating of the catalyst at 150° under pressure in presence of a large amount of water (100 ml) scarcely reduced the activity (Experiment 23). In this case the catalyst was covered with a layer of water, which probably protected it from the deactivating effect of steam. Steam, therefore, is more aggressive in its action than water in the liquid state.

TABLE 6

Deactivation of Raney Nickel Catalyst with Steam under Pressure

Experiment No.	Conditions of steam treatment*			Amounts of hydrogen adsorbed in the first four minutes in the hydrogenation of 0.25 g of phenyl vinyl ether at 20° (ml/min)**
	Pressure (atm)	Temperature (°C)	Duration (hours)	
16	Untreated			28.4—14.8—1.9—0.5
21	37	150	5	10.3— 9.2—8.6—7.1
22	75	150	2	7.5— 7.2—7.2—7.0
23**	4.8	150	2	25.2—17.5—2.7—0.9
24	Untreated ***			19.7—16.1—6.3—2.5
25		100	3	18.9—15.4—6.8—1.4
26		150	3	3.6— 2.3—2.2—2.3

* Amount of catalyst 1 g.

** Catalyst under a layer of water.

*** Another sample of nickel. The moist paste was heated.

Effect of Steam on the Specific Surface of a Mixture of Nickelous Oxide and Alumina

The effect of water vapor on the reduction of nickelous oxide by hydrogen at normal pressure has been studied by several investigators. It was established that water vapor retards the reduction of nickelous oxide, lengthens the induction period, raises the temperature at which reduction begins, and increases the time necessary for complete reduction [6-8]. The inhibiting effect of water vapor on the reduction of metal oxides has been explained by investigators by the formation of a firmly adsorbed film on the metal surface, the oxide surface, or the interface

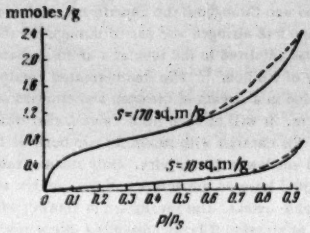

Fig. 1.

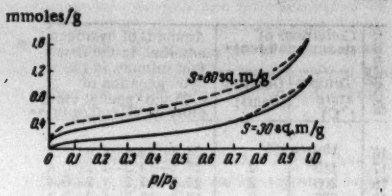

Fig. 2

between the metal and oxide phases. As the degree of reduction of metal oxides (under given conditions of temperature and pressure) depends on the relative concentrations of hydrogen and water vapor in the system, the effect of the latter tends to be equivalent to a change in the thermodynamic conditions of the process, thus resulting in a displacement of equilibrium.

However, this cannot explain the almost complete inertness of nickel prepared by the reduction of steam-tested carrier-supported nickelous oxide. The processes of forming films of adsorbed water vapor, and also oxide films or phases, are reversible. Water vapor may be desorbed, and a metal oxide may be reduced. However, as the results of our experiments show, treatment of nickelous oxide on a carrier with steam under pressure has an irreversible effect on the activity of the catalyst prepared from it.

Our results led us to the view that, in the course of steam treatment, nickelous oxide undergoes extensive recrystallization. In order to verify this we investigated the effect of steam treatment on the specific surfaces of samples No. 7 and 8 of alumina-supported nickelous oxide. A 30-40 mg sample was placed in a high-vacuum apparatus containing a quartz spring balance, and it was freed from adsorbed gases and vapors by treating it for many hours at 250° at a residual pressure of the order of 10^{-5}–10^{-6} mm. Adsorption isotherms were then determined for benzene vapor at 0°. The benzene was first freed from traces of thiophene and moisture and had b.p. 79.7-80° (755 mm) and n_D^{20} 1.5035. The benzene was freed from dissolved air and was thoroughly dried over magnesium perchlorate in the apparatus itself. The pressure of benzene vapor in the system was measured with a mercury manometer accurately within 0.01 mm. The extension of the spirals was measured with a microcatheto-meter accurately within 0.01 mm, which made it possible to determine changes in weight accurately within $1 \cdot 10^{-5}$ g. The surface area was calculated by the Brunauer, Emmett, and Teller method [9] on the assumption that the area of the benzene molecule is 46.5 A^2 [10]. The isotherms for the adsorption of benzene on samples No. 7 and 8 are shown in Figures 1 and 2.

Sample No. 8 of nickelous oxide on alumina was found to be nonporous, and its specific surface was 170 sq.m/g. The specific surface of the same sample after treatment for five hours at 350° with a mixture of steam and hydrogen at pressure of 700 atm was only about 10 sq.m/g; the volume of benzene adsorbed by the sample at saturation was reduced to about one-third by the treatment. The specific surface of sample No. 7 of nickelous oxide on alumina was reduced from 80 to 30 sq.m/g by treatment for five hours at 350° with a mixture of steam and nitrogen. The specific surface of alumina, treated with steam under similar conditions, was reduced by a factor of almost three (from 355 to 125 sq.m/g) [11].

These results confirmed that steam treatment brings about extensive recrystallization both of carrier-supported nickelous oxide and of the carrier itself. They are in accord with the results of van Eyk van Voorthuijsen and Franzen, which show that steam treatment facilitates the perfection of the crystal structure of nickel hydrosilicate [12].

Discussion of Experimental Results

Our results show that catalysts prepared by the reduction of steam-treated nickelous oxide supported on a carrier (Al_2O_3, MgO) are almost completely inactive for the hydrogenation of benzene at normal-pressure; they catalyze the hydrogenation of an ethylene bond (3-octene, styrene) at ordinary pressure, and they will hydrogenate

also an aromatic bond at high pressure [13]. Even after long treatment with hydrogen, the extent to which the nickelous oxide in these catalysts is reduced does not exceed 20-30%. This, however, is does not explain the low activity of catalysts prepared in this way. In our experiments, catalysts (prepared from carrier-supported nickelous oxide which had not been subjected to the action of steam) in which the nickelous oxide was reduced to the extent of, for example, 40-50%,were very active for the hydrogenation of benzene. It is known also that benzene can be readily and completely hydrogenated over a catalyst containing only 1-4% of nickel supported on charcoal [14].

Our adsorption measurements showed that, when treated with steam at high temperature and pressure, a mixture of nickelous oxide and carrier, as also the carrier itself, undergoes far-reaching recrystallization. It appears that the main cause of the inactivity of our catalysts is the low dispersity of the nickel obtained by the reduction of recrystallized nickelous oxide. Lachinov [15] suggested that, owing to the presence of water vapor during reduction with hydrogen under pressure, the iron catalyst for the ammonia synthesis undergoes alternate oxidation and reduction with recrystallization of metal particles and reduction of the activity of the catalyst.

The results that we have obtained on the effect of steam treatment of carrier-supported nickelous oxide on the activity of the catalyst prepared from it enable us to examine the mechanism of the deactivation of metal catalysts by steam in a new light. It was found that steam treatment had the greatest effect on carrier-supported nickelous oxide, and not on reduced nickel. Steam treatment of a prepared nickel catalyst under similar conditions lowered the activity of the catalyst to a much lower extent. When the steam treatment was at ordinary pressure, the difference was difficult to detect, but at high pressure the difference was great. Treatment of carrier-supported nickelous oxide with steam alone had an even greater effect, than treatment with a mixture of steam and hydrogen.

It is clear that the deactivation of the catalyst is due to the recrystallization not of the metal, but of its lower oxide (film or phase), which is formed by the action of steam at high temperature, particularly when the pressure is also high. The subsequent reduction of the coarsely dispersed particles of recrystallized oxide proceeds with great difficulty, being slower and requiring a higher temperature. The metal particles obtained after the reduction of the recrystallized oxide are also of low dispersion and of low activity. We consider that the mechanism that we have proposed is applicable also to the deactivation of iron catalysts by steam.

Kamzolkin and Livshits [16] stated that a few hundredths of a percent of water vapor in the gas mixture lower the productivity of an ammonia-synthesis column by hundreds of kilograms per hour. It is known that it is exceptionally important to have a small admixture of alumina for lasting activity in the iron catalyst of the ammonia synthesis [17]. It may be assumed that, under the action of steam at high temperature, alumia will recrystallize and its promoting effect will be lost. In this lies one of the causes of the deactivation of an iron catalyst by steam.

Shurmovskaya and Bruns [18] consider that in this process at low concentrations of water vapor it is impossible to expect that an iron oxide phase will appear. Reaction of iron is here of a purely surface character. The results of our work show that the deactivating effect of small amounts of water vapor on an iron catalyst can be explained by the formation of a recrystallized, and therefore difficultly reducible, surface film of oxide. The work of Bashkirov and coworkers [19] shows that one of the causes of the irreversible deactivation of an iron catalyst in the synthesis of hydrocarbons from carbon monoxide and hydrogen under pressure is reaction between the water vapor liberated and the catalyst with formation of an iron oxide phase. This conclusion requires supplementation by a demonstration of the occurrence of recrystallization in the metal oxide phase formed by the action of water vapor in a high-pressure system.

SUMMARY

1. An investigation was made into the deactivating effect of steam on nickel catalysts in the course of their preparation by reduction with hydrogen under pressure.

2. It was shown that pretreatment of a mixture of nickelous oxide and carrier (Al_2O_3, MgO) with steam under pressure results in the formation of catalysts of low activity. Similar treatment of a reduced carrier-supported nickel catalyst has a very much smaller effect on activity.

3. It was shown that steam treatment of a coprecipitated mixture of nickelous oxide and alumina (or magnesia) under pressure results in a far-reaching irreversible change, namely recrystallization with great reduction in specific surface.

4. It is evident that the deactivation of reduced nickel catalysts by steam in the course of their use is due to the formation of nickelous oxide films or phases that rapidly recrystallize and are reduced with difficulty with formation of coarsely dispersed nickel. It is probable that the mechanism here proposed is applicable also to the deactivation of iron catalysts by water vapor.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 19. 2-CHLORO-3-BUTENYL- AND 1,3-BUTYADIENYL-PHOSPHONIC ESTERS

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We have previously effected the addition of phosphorus pentachloride to vinyl ethers and to ethylenic and acetylenic hydrocarbons. From the addition products so obtained acid chlorides were prepared by treatment with sulfur dioxide, and these were converted further into other derivatives of unsaturated phosphonic acids [1,2,3]. It was considered to be of interest to investigate the addition reaction between phosphorus pentachloride and dienic hydrocarbons (butadiene, isoprene, piperylene, and 2,3-dimethylbutadiene).

In the present paper we report the synthesis and reactions of 2-chloro-3-butenylphosphonic dichloride. This substance was prepared as follows:

$$CH_2=CH-CH=CH_2+2PCl_5\rightarrow CH_2=CH-CHCl-CH_2PCl_4PCl_5;$$
$$CH_2=CH-CHCl-CH_2PCl_4\cdot PCl_5+2SO_2\rightarrow CH_2=CH-CHCl-CH_2POCl_2+$$
$$+POCl_3+2SOCl_2.$$

From the ozonization products of the acid chloride obtained, formic acid was isolated. This gave us reason to believe that addition of phosphorus pentachloride to butadiene occurs at the 1,2-position. 2-Chloro-3-butenylphosphonic dichloride is a colorless liquid having the characteristic odor of an acid chloride. It readily reacts with alcohols and is soluble in all organic solvents. By the use of the very vigorous reaction of 2-chloro-3-butenylphosphonic dichloride with alcohols, we were able to synthesize 2-chloro-3-butenylphosphonic esters by the method of Milobendzski and Sachnowski [4]:

$$CH_2=CH-CHCl-CH_2POCl_2+2ROH+2C_5H_5N\rightarrow$$
$$\rightarrow CH_2=CH-CHCl-CH_2PO(OR)_2+2C_5H_5N\cdot HCl.$$

In this way we prepared the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, allyl, hexyl, 2-methoxyethyl, and 2-ethoxyethyl esters of 2-chloro-3-butenylphosphonic acid.

2-Chloro-3-butenylphosphonic esters are colorless mobile liquids, readily distilled under reduced pressure, and soluble in the usual organic solvents. They decolorize bromine water and give a positive Beilstein test for chlorine. The constants of these esters are given in Table 1.

When the 2-chloro-3-butenylphosphonic esters were treated with alcoholic potash, hydrogen chloride was eliminated and the corresponding 1,3-butadienylphosphonic esters were formed in accordance with the reaction

$$CH_2=CH-CHCl-CH_2PO(OR)_2+\xrightarrow[C_2H_5OH]{KOH}CH_2=CH-CH=CHPO(OR)_2+$$
$$+KCl.$$

TABLE 1

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield of ester (%)	Phosphorus content (%) found	Phosphorus content (%) calculated
1	$CH_2=CH-CHCl-CH_2\cdot PO(OCH_3)_2$	112—114 (2)	1.4770	1.2365	50	15.59; 15.45	15.61
2	$CH_2=CH-CHCl-CH_2\cdot PO(OC_2H_5)_2$	122.5—123.5 (3)	1.4672	1.1532	52	13.42; 13.31	13.68
3	$CH_2=CH-CHCl-CH_2\cdot PO(OC_3H_7\text{-}n)_2$	121—123 (1)	1.4650	1.1011	65	11.74; 11.95	12.18
4	$CH_2=CH-CHCl-CH_2\cdot PO(OC_3H_7\text{-}i)_2$	113—116 (2)	1.4585	1.0845	44	12.07; 11.98	12.18
5	$CH_2=CH-CHCl-CH_2\cdot PO(OC_4H_9\text{-}n)_2$	147 (2)	1.4625	1.0634	62	10.72; 10.64	10.97
6	$CH_2=CH-CHCl-CH_2\cdot PO(OC_4H_9\text{-}i)_2$	124—126 (2)	1.4608	1.0504	67	10.70; 10.89	10.97
7	$CH_2=CH-CHCl-CH_2\cdot PO(OC_5H_9)_2$	135 (2)	1.4832	1.1476	60	12.34; 12.26	12.36
8	$CH_2=CH-CHCl-CH_2\cdot PO(OC_8H_{17}\text{-}n)_2$	160—162 (1)	1.4628	1.0158	58	9.10; 9.07	9.15
9	$CH_2=CH-CHCl-CH_2\cdot PO(OCH_2-CH_2-OCH_3)_2$	157—160 (2)	1.4720	1.1844	50	10.79; 10.79	10.82
10	$CH_2=CH-CHCl-CH_2\cdot PO(OCH_2-CH_2-OC_2H_5)_2$	165—167 (2)	1.4700	1.1348	62	10.12; 10.13	9.85

TABLE 2

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield of ester (%)	Phosphorus content (%) found	Phosphorus content (%) calculated
1	$CH_2=CH-CH=CHPO(OCH_3)_2$	77—78.5 (3)	1.4835	1.1021	60	18.97; 18.85	19.13
2	$CH_2=CH-CH=CHPO(OC_2H_5)_2$*	84—87 (2)	1.4728	1.0465	75	15.94; 15.86	16.03
3	$CH_2=CH-CH=CHPO(OC_3H_7\text{-}n)_2$	103—104 (1)	1.4700	1.0163	90	13.89; 13.97	14.22
4	$CH_2=CH-CH=CHPO(OC_3H_7\text{-}i)_2$	83—84.5 (2)	1.4632	1.0030	87	13.86; 13.82	14.22
5	$CH_2=CH-CH=CHPO(OC_4H_9\text{-}n)_2$	129 (2)	1.4680	0.9922	65	12.23; 12.33	12.60
6	$CH_2=CH-CH=CHPO(OC_4H_9\text{-}i)_2$	111—113 (2)	1.4642	0.9819	86	12.61; 12.59	12.60
7	$CH_2=CH-CH=CHPO(OC_5H_9)_2$	98—100 (2)	1.4872	1.0541	81	14.02; 14.17	14.00
8	$CH_2=CH-CH=CHPO(OC_8H_{17}\text{-}n)_2$	150—153 (2)	1.4600	0.9839	48	9.83; 9.95	10.02
9	$CH_2=CH-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	135—138 (2)	1.4775	1.1287	46	12.20; 12.42	12.40
10	$CH_2=CH-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	145—147 (2)	1.4690	1.0954	43	10.96; 10.82	11.15

* According to a patent [5], diethyl 1,3-butadienylphosphonate, b.p. 100-124° (11 mm), was prepared by reaction between phosphorus pentachloride and butadiene with subsequent treatment of the tetrachloride with alcohol, the product being then dehydrochlorinated with alcoholic potash.

In this way we prepared and characterized the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, allyl, hexyl, 2-methoxyethyl, and 2-ethoxyethyl esters of 1,3-butadienylphosphonic acid. All these esters are colorless liquids that can be readily distilled under reduced pressure. They combine with bromine with formation of thick sirups, which do not crystallize and which decompose when vacuum-distilled. Constants of 1,3-butadienylphosphonic esters are given in Table 2.

EXPERIMENTAL

2-Chloro-3-butenylphosphonic Dichloride $CH_2=CH-CHCl-CH_2-POCl_2$. A mixture of 208 g of phosphorus pentachloride and 250 ml of absolute benzene was prepared in a three-necked flask fitted with mechanical stirrer, condenser, and tube for the passage of gas. The mixture was cooled with ice and stirred while 85-90 g of 1,3-butadiene was passed in. A yellowish crystalline mass formed and was left overnight. On the next day the crystalline butadiene-PCl_5 addition product was treated with sulfur dioxide until complete dissolution occurred. After removal of solvent, thionyl chloride, and phosphoryl chloride by distillation, the residue was vacuum-fractionated at a residual pressure of 2 mm.

The yield of acid chloride, m.p. 103-105° (2 mm), n_D^{20} 1.5200; d_4^{20} 1.4452 was 114 g (90%).

Found %: C 23.05, 23.14; H 2.83, 2.94; P 14.85, 14.82; Cl 51.48, 51.20. $C_4H_6POCl_3$. Calculated %: C 23.13; H 2.89; P 14.93; Cl 51.32.

Ozonization of 2-Chloro-3-butenylphosphonic Dichloride. A solution of 10 g of 2-chloro-3-butenylphosphonic dichloride, b.p. 103-105° (2 mm), in chloroform was treated with ozone at 0° for 12 hours (ozone concentration 5%). Water (25 ml) and 5% hydrogen peroxide (7 ml) were added to the solution of ozonide. The mixture was heated for nine hours at 65°, and was then neutralized with 10 g of sodium carbonate. After the separation of chloroform, the solution of water-soluble salts was vacuum-evaporated to dryness. The residue was decomposed with 5% hydrochloric acid and extracted several times with ethyl ether. After removal of ether, formic acid, b.p. 98-100° and n_D^{20} 1.3720, was isolated (the literature [6] gives b. p. 100.8° and n_D^{20} 1.3714). There was a positive calomel reaction for formic acid. The formic acid was distilled from the mixture of water-soluble acids, and a dark-brown resin remained. This did not crystallize, even after a long time, and it decomposed when attempts were made to distil it in a vacuum. Nothing could be isolated from the chloroform solution.

Dimethyl 2-Chloro-3-butenylphosphonate $CH_2=CH-CHCl-CH_2PO(OCH_3)_2$. A mixture of 75 ml of of benzene, 12.8 g of absolute methanol, and 31.6 g of pyridine was prepared in a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. The mixture was cooled with ice water and stirred while 41.5 g of 2-chloro-3-butenylphosphonic dichloride was added gradually. When the whole of the acid chloride had been added, the reaction mixture was set aside overnight. On the next day the mixture was heated for two hours at 75-80° and then cooled. Pyridine hydrochloride was filtered off, and the filtrate was dried over sodium sulfate. After removal of solvent, the residue was vacuum-fractionated and gave 20 g (50%) of the ester, b.p. 112-114° (2 mm), n_D^{20} 1.4770, and d_4^{20} 1.2365.

Found %: P 15.59, 15.45. $C_6H_{12}PO_3Cl$. Calculated %: P 15.61.

All the other 2-chloro-3-butenylphosphonic esters were prepared in the same way.

Dimethyl 1,3-Butadienylphosphonate $CH_2=CH-CH=CHPO(OCH_3)_2$. A solution of 1.8 g of caustic potash in 20 ml of absolute alcohol was placed in a flask fitted with stirrer, condenser, and dropping funnel. The solution was stirred while 6.5 g of dimethyl 2-chloro-3-butenylphosphonate was added. After the addition of the whole of the ester, the reaction mixture was heated for two hours at 70°. When the mixture was cool, potassium chloride was filtered off and alcohol was distilled from the filtrate. Vacuum fractionation of the residue gave 3.5 g of dimethyl 1,3-butadienylphosphonate, b.p. 77-78.5° (3 mm), n_D^{20} 1.4835, and d_4^{20} 1.1021.

Found %: P 18.97, 18.85. $C_6H_{11}PO_3$. Calculated %: P 19.13.

The other 1,3-butadienylphosphonic esters were synthesized in a similar way.

SUMMARY

1. With the aid of the addition reaction between phosphorus pentachloride and 1,3-butadiene, 2-chloro-3-butenylphosphonic dichloride was prepared.

2. The methyl, ethyl, propyl, isopropyl, butyl, isobutyl, allyl, hexyl, 2-methoxyethyl, and 2-ethoxyethyl esters of 2-chloro-3-butenylphosphonic acid were prepared by the action of alcohols on 2-chloro-3-butenylphosphonic dichloride, and some of their properties were determined.

3. By reaction between alcoholic potash and esters of 2-chloro-3-butenylphosphonic acid, the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, allyl, hexyl, 2-methoxyethyl, and 2-ethoxyethyl esters of 1,3-butadienylphosphonic acid were synthesized.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 20. 2-CHLORO-3-METHYL-3-BUTENYL- AND 3-METHYL-1,3-BUTADIENYL-PHOSPHONIC ESTERS

K. N. Anisimov and N. E. Kolobova

In the preceding communication [1] we described the addition of phosphorus pentachloride to 1,3-butadiene. With the aid of this reaction we prepared 2-chloro-3-butenylphosphonic dichloride, 2-chloro-3-butenylphosphonic esters, and 1,3-butadienylphosphonic esters. In continuation of our investigations on the addition of phosphorus pentachloride to dienic hydrocarbons, we have studied the addition of phosphorus pentachloride to isoprene.

The process was carried out under the conditions described in the preceding paper [1], the reactions occurring being

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2+2PCl_5\rightarrow CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CHCl-CH_2PCl_4\cdot PCl_5;$$

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH-CH_2\cdot PCl_4\cdot PCl_5+2SO_2\rightarrow CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}H-CHCl-CH_2POCl_2+POCl_3+2SOCl_2$$

The position at which the addition of phosphorus pentachloride to isoprene occurred was determined by ozonization of the acid chloride obtained. Formic acid was isolated from the ozonolysis products, which gave us reason to believe that addition to isoprene occurred at the 1,2-position, so that the product was 2-chloro-3-methyl-3-butenylphosphonic dichloride.

Treatment of this substance with alcohols gave diesters of 2-chloro-3-methyl-3-butenylphosphonic acid, in accordance with the reaction [2]:

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CHCl-CH_2POCl_2+2ROH+2C_5H_5N\longrightarrow$$

$$\longrightarrow CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CHCl-CH_2PO(OR)_2+2C_5H_5N\cdot HCl$$

Constants of the esters obtained are given in Table 1.

2-Chloro-3-methyl-3-butenylphosphonic esters are readily dehydrochlorinated by alcoholic potash with formation of 3-methyl-1,3-butadienylphosphonic esters:

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CHCl-CH_2PO(OR)_2+\xrightarrow[C_2H_5O]{KOH}$$

$$\rightarrow CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CHPO(OR)_2+KCl$$

TABLE 1

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield of ester (%)	Phosphorus content (%) found	Phosphorus content (%) calculated
1	$CH_2=C(CH_3)-CHCl-CH_2PO(OCH_3)_2$	119—121 (3)	1.4805	1.1971	50	14.84; 14.76	14.58
2	$CH_2=C(CH_3)-CHCl-CH_2PO(OC_2H_5)_2$	134—135 (5)	1.4698	1.1237	84	13.03; 13.25	12.88
3	$CH_2=C(CH_3)-CHCl-CH_2PO(OC_3H_7\text{-}n)$	136—137 (3)	1.4668	1.0829	73	11.26; 11.45	11.54
4	$CH_2=C(CH_3)-CHCl-CH_2PO(OC_3H_7\text{-}i)_2$	127—128 (2)	1.4618	1.0712	70	11.56; 11.52	11.54
5	$CH=C(CH_3)-CHCl-CH_2PO(OC_4H_9\text{-}n)_2$	140—141 (1)	1.4665	1.0530	75	10.54; 10.64	10.45
6	$CH_2=C(CH_3)-CHCl-CH_2PO\,OC_4H_9\text{-}i)_2$	141—142 (3)	1.4639	1.0456	83	10.34; 10.64	10.45
7	$CH_2=C(CH_3)-CHCl-CH_2PO(OC_5H_5)_2$	143—144 (2)	1.4870	1.1137	52	11.88; 11.79	11.72
8	$CH_2=C(CH_3)-CHCl-CH_2PO(OC_6H_{13}\text{-}n)_2$	160—162 (2)	1.4642	1.0043	61	9.20; 9.22	8.79
9	$CH_2=C(CH_3)-CHCl-CH_2PO(OCH_2-CH_2-OCH_3)_2$	148—150 (2)	1.4738	1.1370	55	10.76; 10.76	10.31
10	$CH=C(CH_3)-CHCl-CHPO(OCH_2-CH_2-OC_2H_5)_2$	155—157 (2)	1.4672	1.0981	50	9.86; 9.89	9.43

TABLE 2

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield of ester (%)	Phosphorus content (%) found	Phosphorus content (%) calculated
1	$CH_2=C(CH_3)-CH=CHPO(OCH_3)_2$	95—96 (3)	1.4868	1.1015	74	17.42; 17.46	17.61
2	$CH_2=C(CH_3)-CH=CHPO(OC_3H_6)_2$[3]	93—95 (2)	1.4768	1.0415	85	15.77; 15.85	15.99
3	$CH_2=C(CH_3)-CH=CHPO(OC_4H_7\text{-}n)_2$	127—128 (3)	1.4728	1.0108	81	13.20; 13.45	13.36
4	$CH_2=C(CH_3)-CH=CHPO(OC_4H_7\text{-}n)_2$	93—94 (2,5)	1.4660	0.9911	79	13.36; 13.22	13.36
5	$CH_2=C(CH_3)-CH=CHPO(OC_4H_9\text{-}n)_2$	118—119 (1)	1.4711	0.9854	84	12.29; 12.32	11.92
6	$CH_2=C(CH_3)-CH=CHPO(OC_4H_9\text{-}i)_2$	138—139 (5)	1.4678	0.9781	78	12.06; 12.08	11.92
7	$CH_2=C(CH_3)-CH=CHPO(OC_6H_5)_2$	124—125 (2)	1.4936	1.0490	86	13.75; 13.87	13.59
8	$CH_2=C(CH_3)-CH=CHPO(OC_6H_{13}\text{-}n)_2$	137—138 (3)	1.4678	0.9588	60	10.25; 10.25	9.81
9	$CH_2=C(CH_3)-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	151—152 (3)	1.4798	1.0978	47	11.32; 11.38	11.74
10	$CH_2=C(CH_3)-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	154—155 (1)	1.4705	1.0670	49.5	11.03; 11.04	10.65

Properties of 3-methyl-1,3-butadienylphosphonic esters are given in Table 2.

EXPERIMENTAL

Preparation of 2-Chloro-3-methyl-3-butenylphosphonic Dichloride $CH_2=C(CH_3)-CHCl-CH_2POCl_2$. A mixture of 500 ml of benzene and 417 g (2 moles) of phosphorus pentachloride was prepared in a three-necked flask fitted with mechanical stirrer, dropping funnel, and reflux condenser. The mixture was cooled with ice water and stirred well while 74.8 g (1.1 moles) of isoprene was added gradually. The crystalline addition product formed was left ovemight and then treated with sulfur dioxide until it was converted completely into a liquid. Solvent, thionyl chloride, and phosphoryl chloride were distilled off. Vacuum fractionation of the residue gave 200 g (90%) of 2-chloro-3-methyl-3-butenylphosphonic dichloride, b.p. 107-108° (2 mm), n_D^{20} 1.5230; d_4^{20} 1.3918.

Found %: C 27.19, 27.25; H 3.81, 3.72; P 13.92, 13.98; Cl 47.82, 47.73. $C_5H_9POCl_3$. Calculated %: C 27.08; H 3.61; P 13.99; Cl 48.08.

Synthesis of Dimethyl 2-Chloro-3-methyl-3-butenylphosphonate $CH_2=C(CH_3)-CHCl-CH_2PO(OCH_3)_2$. A mixture of 150 ml of benzene, 16 g (0.5 mole) of methanol, and 39.5 g (0.5 mole) of pyridine was prepared in a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. The mixture was cooled with ice water and stirred while 55.3 g (0.25 mole) of 2-chloro-3-methyl-3-butenylphosphonic dichloride was added gradually. On the next day the reaction mixture was heated for two hours at 70°, and then cooled. The precipitate of pyridine hydrochloride was filtered off, and the filtrate was washed with 3% sodium carbonate solution and dried over magnesium sulfate. The solvent was distilled off, and vacuum fractionation of the residue gave 27.4 g (50%) of product, b.p. 119-121° (3 mm), n_D^{20} 1.4805; d_D^{20} 1.1971.

Found %: P. 14.84, 14.76. $C_7H_{14}PO_3Cl$. Calculated %: P 14.58.

All the other 2-chloro-3-methyl-3-butenylphosphonic esters were prepared by this method.

Preparation of Dimethyl 3-Methyl-1,3-butadienylphosphonate $CH_2=C(CH_3)-CH=CHPO(OCH_3)_2$. A solution of 5.4 g (0.1 mole) of caustic soda in 50 ml of absolute ethanol was placed in a three-necked flask fitted with stirrer, condenser, and dropping funnel. The solution was stirred while 21.2 g (0.1 mole) of dimethyl 2-chloro-3-methyl-3-butenylphosphonate was added slowly. The reaction mixture was then heated at 80° for three hours. The potassium chloride that was precipitated was filtered off, alcohol was distilled off, and vacuum distillation of the residue gave 13 g (74%) of the ester, b.p. 95-96° (2 mm), n_D^{20} 1.4868; d_4^{20} 1.1015.

Found %: P 17.42, 17.46. $C_7H_{13}PO_3$. Calculated %: P 17.61.

The other 3-methyl-1,3-butadienylphosphonic esters listed in Table 2 were prepared similarly.

SUMMARY

1. With the aid of the reaction between isoprene and phosphorus pentachloride, 2-chloro-3-methyl-3-butenylphosphonic dichloride was prepared.

2. The methyl, ethyl, propyl, isopropyl, butyl, isobutyl, allyl, hexyl, 2-methoxyethyl, and 2-ethoxyethyl esters of 2-chloro-3-methyl-3-butenylphosphonic and 3-methyl-1,3-butadienylphosphonic acids were prepared and characterized.

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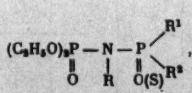
ALKYLAMIDES OF ORGANIC DERIVATIVES OF PHOSPHORUS ACIDS

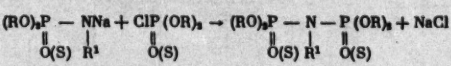
B. A. Arbuzov, P. I. Alimov and O. N. Fedorova

In the preceding communication [1] we described the synthesis of organic derivatives of bis[phosphoric acid] amide of general formula



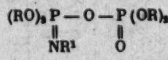
in which R^1 is C_2H_5O or $(CH_3)_2N$, R^2 is C_2H_5O or $(CH_3)_2N$, and R is CH_3, C_2H_5, C_4H_9, or C_6H_5. Tests on toxicity to the corn weevil showed that these compounds have insecticidal properties, their activities being determined both by the radicals attached to phosphorus and by the radicals attached to nitrogen.

In order to extend the range of these organic compounds of phosphorus and nitrogen, improve the method of preparation, study their physical and chemical properties and also physiological activity, we synthesized amides of phosphorus acids, analogous to the above, but with different groups on the phosphorus and nitrogen atoms. These substances were synthesized by reaction of phosphorochloridic esters and their thiono analogs with N-alkyl-N-sodiophosphoramidic esters and their thiono analogs in accordance with the equation.



in which R is C_3H_7, i-C_3H_7, C_4H_9, or i-C_4H_9, and R^1 is CH_3 or C_2H_5; OR may be replaced by $(CH_3)_2N$. N-Alkyl-N-sodiophosphoramidic esters are readily soluble in organic solvents (ether and gasoline).

Apart from the structure given above, the following could be proposed for the compounds synthesized:



This structure, however, is less probable.

Table 1 gives the formulas, physical constants, yields, and results of the elementary analysis of the alkylamides prepared in this way. The compounds listed in this table are colorless mobile liquids having a feeble ethereal odor. They are readily soluble in organic solvents, but sparingly soluble in water. In tests on the corn weevil they showed rather low insecticidal activity. For example, compound No. 4 – the tetraisopropyl ester of bis[phosphoric acid] methylamide – gave a mortality figure of 8% of the beetles in one day for a concentration of 0.2%.

TABLE 1

No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Phosphorus content (%) found		Phosphorus content (%) calculated	Yield (%)
1	$(C_2H_7O)_2P(O)-N(CH_2O)-P(OC_2H_7)_2$	159—160 (2)	1.4365	1.0867	86.76	86.77	17.33	17.18	17.27	30.41
2	$(i\text{-}C_3H_7O)_2P(O)-N(CH_2)-P(O)(OC_3H_7\text{-}i)_2$	128—129 (2)	1.4292	1.0686	86.64	86.77	17.42		17.27	46.81
3	$(C_2H_7O)_2P(O)-N(C_2H_5O)-P(O)(C_2H_7O)_2$	160—161 (1)	1.4385	1.0746	91.21	91.39	16.91;	16.72	16.62	51.06
4	$(i\text{-}C_3H_7O)_2P(O)-N(C_2H_5O)-P(O)(OC_3H_7\text{-}i)_2$	129—130 (1)	1.4288	1.0612	90.58	91.39	16.86;	17.00	16.62	48
5	$(i\text{-}C_4H_9O)_2P(O)-N(CH_2O)-P(O)(OC_4H_9\text{-}i)_2$	162—163 (2)	1.4375	1.0335	105.3	105.24	15.23;	15.25	14.94	54.68
6	$(C_4H_9O)_2P(O)-N(C_2H_5O)-P(O)(OC_4H_9)_2$	173—174 (1)	1.4411	1.0398	109.0	109.86	14.68;	14.36	14.46	45.67
7	$(i\text{-}C_4H_9O)_2P(O)-N(C_2H_5O)-P(O)(OC_4H_9\text{-}i)_2$	157—158 (1)	1.4370	1.0264	109.5	109 86	14.63;	14.50	14.46	57.4
8	$(CH_3)_2N-P(O)(OC_2H_5)-N(C_2H_5O)-P(O)(OC_2H_5)-N(CH_3)_2$	140—142 (2)	1.4560	1.1214	76.36	76.29	19.83;	19.83	19.68	39.92

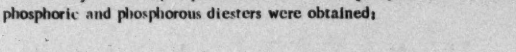
TABLE 1 (continued)

No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Phosphorus content (%) found		Phosphorus content (%) calculated	Yield (%)
9	$(i\text{-}C_3H_7O)_2P(O)-N(CH_3)-P(S)(OC_3H_7\text{-}i)_2$	126—127.5 (1)	1.4535	1.0786	94.06	94.26	16.76;	16.50	16.53	64.02
10	$(C_3H_7O)_2P(O)-N(C_2H_5)-P(S)(OC_3H_7)_2$	142—144 (1)	1.4570	1.7044	98.61	98.87	16.15	16.18	15.94	47.62
11	$(C_2H_5O)_2P(S)-N(CH_3)-P(S)(OC_2H_5)_2$	134—135 (1.5)	1.4940	1.1662	83.63	83.27	18.82	18.56	18.50	30.35
12	$C_2H_5O)_2P(S)-N(C_2H_5)-P(S)(OC_2H_5)_2$	133—134 (1)	1.4913	1.1476	88.13	87.89	18.19	18.00	17.76	8.0

TABLE 2

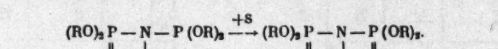
No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Phosphorus content (%) found		Phosphorus content (%) calculated	Yield (%)
1	$(C_2H_5O)_2P(O)-N(CH_3)-P(OC_2H_5)_2$	104—106 (1)	1.4435	1.1045	68.95	69.37	21.36	21.35	21.6	43.4
2	$(i\text{-}C_3H_7O)_2P(O)-N(CH_3)-P(OC_3H_7\text{-}i)$	107—109 (1)	1.4330	1.0179	87.58	87.85	18.04	18.00	18.07	44.86
3	$(C_3H_7O)_2P(O)-N(C_2H_5)-P(OC_3H_7)_2$	126—127 (1)	1.4405	1.0213	92.21	92.46	17.38	17.50	17.37	40

By reaction between N-alkyl-N-sodiophosphoramidic esters and phosphorochloridous esters, alkylamides containing residues of phosphoric and phosphorous diesters were obtained:

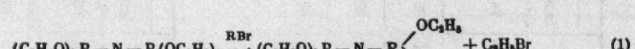


in which R is C_2H_5, i-C_3H_7, or C_3H_7, and R^1 is CH_3 or C_2H_5. The constants of substances synthesized in this way are given in Table 2.

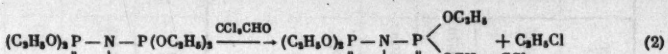
Tetraalkyl esters of mixed alkylamides of phosphoric and phosphorous acids, being compounds containing a tervalent phosphorus atom, are able to undergo addition reactions and rearrangement of ester groupings at the tervalent phosphorus atom. Thus they readily combine with sulfur with formation of mixed alkylamides of phosphoric and phosphorothionic acids:



When treated with alkyl halides, the alkylamides isomerize or undergo rearrangement into compounds containing two quinquevalent phosphorus atoms:

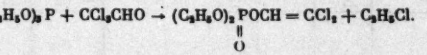


(1)



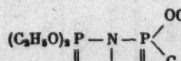
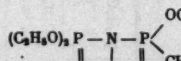
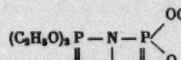
(2)

The last compound is assigned its structure by analogy with the structure of the substance obtained by reaction of chloral with triethyl phosphite [2]:



The constants of substances obtained by these isomerization and rearrangement reactions are given in Table 3.

TABLE 3

No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated
1		132—133 (1)	1.4430	1.1394	66.78	67.17
2		161—163 (1)	1.4490	1.1878	77.92	78.00
3		152—153 (1)	1.4606	1.3077	77.56	77.56

EXPERIMENTAL

I. Synthesis of Tetraalkyl Esters of Bis[phosphoric acid] Alkylamides

Tetrapropyl Ester of Bis[phosphoric acid] Methylamide. Dipropyl Phosphorochloridate (26.06 g, i.e. 0.13 mole) was added to a cooled stirred solution of dipropyl N-methyl-N-sodiophosphoramidate prepared from 25.35 g (0.13 mole) of the N-methylphosphoramidic ester and 3 g (0.13 g-atom) of sodium in 120 ml of gasoline, b.p. 70-120°. When addition was complete, the mixture was heated for one hour at 55-65° and then left overnight. Sodium chloride was removed by centrifugation, and gasoline was distilled off under reduced pressure. The residue, which amounted to 38.5 g (82.4%), was distilled at 2 mm from an Arbuzov flask, and the following fractions were obtained:

Fraction I, b. p. 95-165°; 10.2 g
Fraction II, b.p. 165-171°; 18.2 g
Residue 9.0 g

Redistillation of Fraction II gave 14.2 g (30.4%) of a substance having b.p. 159-160° (1 mm); n_D^{20} 1.4365; d_4^{20} 1.0867; found MR 86.46; calculated $C_{13}H_{31}O_6P_2N$ MR 86.77.

Found %: P 17.33, 17.18. $C_{13}H_{31}O_6P_2N$. Calculated %: P 17.22.

The product was a colorless mobile liquid, readily soluble in organic solvents. Compounds No. 2, 3, 4, 5, 6, 7, 8, 11, and 12 in Table 1 were prepared under similar conditions.

II. Synthesis of Tetraalkyl Esters of Mixed Alkylamides of Phosphoric and Phosphorous Acids

Tetraisopropyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids. This compound was prepared by the action of 10.3 g (0.056 mole) of diisopropyl phosphorochloridite on diisopropyl N-methyl-N-sodiophosphoramidate, prepared from 10.9 g (0.056 mole) of the N-methylphosphoramidic ester and 1.28 g (0.056 g-atom) of sodium in 100 ml of gasoline. The crude product, amounting to 17.5 g (91.3%), was distilled at 2 mm, and the following fractions were obtained:

Fraction I, b.p. 45-110°; 2.5 g
Fraction II, b.p. 110-115°; 12.5 g
Residue 1.5 g

Redistillation of Fraction II gave 8.6 g (44.8%) of a substance having b.p. 107-109° (1 mm); n_D^{20} 1.4330; d_4^{20} 1.0179; found MR 87.58; calculated $C_{13}H_{31}O_5P_2N$ MR 87.91.

Found %: P 18.04, 18.00. $C_{13}H_{31}O_5P_2N$. Calculated %: P 18.07.

This substance is a colorless mobile liquid having a feeble odor reminiscent of a phosphorous ester; it is readily soluble in organic solvents. Compounds No. 1 and 3 in Table 2 were prepared similarly.

III. Synthesis of Tetraalkyl Esters of Mixed Alkylamides of Phosphoric and Phosphorothionic Acids

Addition of Sulfur to the Tetraisopropyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids. A mixture of 5.6 g of the methylamide (b.p. 107-109° (1 mm)), 0.52 g of sulfur (1 g-atom per mole of amide), and 25 ml of benzene was heated at the boiling point of benzene for 20 minutes. Solvent was distilled off, and the residue was vacuum-distilled. The main fraction, amounting to 3.9 g (64.2%), had b.p. 126-127.5° (1 mm); n_D^{20} 1.4535; d_4^{20} 1.0786; found MR 94.08; calculated $C_{13}H_{31}O_5P_2NS$ MR 94.28. Compounds No. 9 and 10 in Table 1 were prepared similarly.

Found %: P 16.76, 16.5; S 8.32, 8.29. $C_{13}H_{31}O_5P_2NS$. Calculated %: P 16.53; S 8.53.

IV. Action of Halogen Compounds on the Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids

Isomerization of the Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids with Ethyl Iodide. A mixture of 7 g of the amide (b.p. 104-106° (1 mm)) and 1 g of ethyl iodide was sealed in a glass tube and heated for six hours at 120-130°. Distillation of the contents of the tube gave a main

fraction amounting to 4.5 g (64.3%) and having b.p. 132-133° (1 mm), n_D^{20} 1.4430; d_4^{20} 1.1394; found MR 66.78; calculated $C_9H_{19}O_5P_2N$ MR 66.67.

Found %: P 21.82, 21.73. $C_9H_{19}O_5P_2N$. Calculated %: P 21.60.

The substance was a colorless liquid, readily soluble in organic solvents.

Action of Ethyl Bromoacetate on the Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids. The amide (10 g, i.e. 0.035 mole) was heated to 120°, and 5.8 g (0.035 mole) of ethyl bromoacetate was added from a dropping funnel. The mixture was heated for one hour at 120-130°. Distillation gave a main fraction amounting to 6.5 g (67.6%) and having b.p. 161-163° (1 mm); n_D^{20} 1.4490; d_4^{20} 1.1878; found MR 77.92; calculated $C_{11}H_{25}O_7P_2N$ MR 78.06.

Found %: P 17.71, 18.00. $C_{11}H_{25}O_7P_2N$. Calculated %: P 17.97.

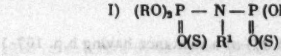
The product was a feebly smelling colorless liquid, soluble in organic solvents.

Action of Chloral on the Tetraethyl Ester of the Mixed Methylamide of Phosphoric and Phosphorous Acids. Chloral (4.7 g, i.e. 0.032 mole) was added from a dropping funnel at room temperature to 9.18 g (0.032 mole) of the amide. Reaction was accompanied by rise in temperature and liberation of ethyl chloride. When reaction was complete, the crude product was vacuum-distilled. A fraction, amounting to 7.8 g (65.5%), came over at 152-153° (1 mm); it had n_D^{20} 1.4606; d_4^{20} 1.3077; found MR 77.56; calculated $C_9H_{19}O_6P_2NCl_2$ MR 77.56.

Found %: P 17.11, 17.10. $C_9H_{19}O_6P_2NCl_2$. Calculated %: P 16.76.

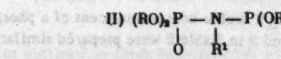
SUMMARY

1. By reaction of phosphorochloridic esters (and their thiono analogs) and of phosphorochloridous esters with N-alkyl-N-sodiophosphoramidic esters (and their thiono analogs), organic compounds of phosphorus and nitrogen of the following general formulas were synthesized:



I) $(RO)_2P(O(S))-N(R^1)-P(O(S))(OR)_2$,

in which R is C_3H_7, i-C_3H_7, C_4H_9, or i-C_4H_9, and R^1 is CH_3 or C_2H_5; OR may be replaced by $(CH_3)_2N$;



II) $(RO)_2P(O)-N(R^1)-P(OR)_2$,

in which R is C_2H_5, C_3H_7, or i-C_3H_7, and R^1 is CH_3 or C_2H_5.

2. Physical constants of these products were determined, some of their chemical properties were investigated, and they were examined for insecticidal activity.

LITERATURE CITED

[1] B. A. Arbuzov, P. I. Alimov, M. A. Zvereva et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 1047-1052 (T.p. 913).*

[2] W. Perkow, Ber. 87, 755 (1954).

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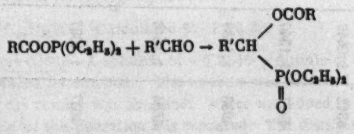
* T.p. = C. B. Translation pagination.

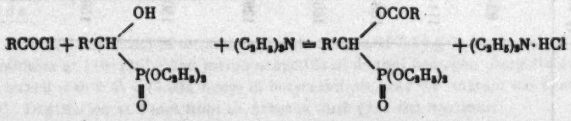
ACYL DERIVATIVES OF 1-HYDROXYALKYLPHOSPHONIC ESTERS

P. I. Alimov and I. V. Cheplanova

In studying the properties of mixed anhydrides derived from diethyl hydrogen phosphite and a carboxylic acid $RCOOP(OC_2H_5)_2$ [1], we found that these compounds readily react with aldehydes with formation of acyl derivatives of 1-hydroxyalkylphosphonic esters:



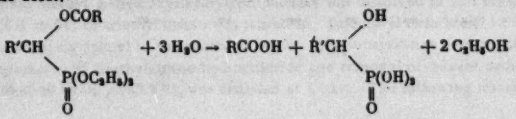
As organophosphorus compounds of this series were not known previously, in the present paper we give data on their properties and describe a more convenient method for their preparation. Synthesis by the second method is effected by reaction of acid chlorides in presence of triethylamine with 1-hydroxyalkylphosphonic esters having a hydrogen on the 1-carbon atom:



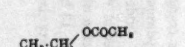
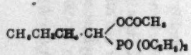
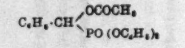
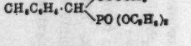
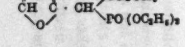
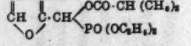
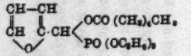
The reaction was carried out in gasoline solution at room temperature and it was completed by heating the mixture at 50-60° for 60-90 minutes. 1-Hydroxyalkylphosphonic esters in which the hydrogen on the 1-carbon was replaced by a radical were found to be much less active toward the acid chloride. Under the conditions described above, acyl derivatives of these esters are either not formed at all, or are formed in very low yield. Reaction under more severe conditions gives somewhat higher yields. Thus, when a xylene solution of acetyl chloride, diethyl 1-hydroxy-1-methylethylphosphonate, and triethylamine was heated at 80-90° for 13 hours, the product was a mixture, b.p. 95-96° (0.5 mm), consisting of the acetyl derivative of diethyl 1-hydroxy-1-methylethylphosphonate (43%) and unchanged hydroxy ester.

The diethyl 1-hydroxyalkylphosphonates were prepared by Abramov's method [2]. The table gives constants and yields of the 1-(acyloxy)alkylphosphonic esters that we synthesized.

The substances listed in the table are colorless or yellowish liquids which can be distilled in a vacuum without decomposition. When boiled with 10% caustic soda they are hydrolyzed with formation of carboxylic and 1-hydroxyalkylphosphonic acids:



TABLE

No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Phosphorus content (%) found	Phosphorus content (%) calculated	Yield (%)
1		93—93.5 (0.5)	1.4271	1.1083	51.9	51.67	13.94; 13.87	13.83	76.8
2		111—112 (2)	1.4312	1.0649	61.28	60.9	12.53; 12.51	12.30	50.9
3		158—160 (2)	1.4917	1.1540	71.86	71.15	11.00; 11,19	10.8	55.6
4		168—169 (3)	1.4933	1.1333	76.97	75.77	10.33; 10,23	10.33	64
5		129—130 (0.5)	1.4694	1.1946	64.39	64.60	11.21; 11.18	11.23	39.1
6		150—151 (1.5)	1.4637	1.1387	73.62	73.83	10.36; 10,07	10.2	67
7		156—157 (0.5)	1.4640	1.1088	82.65	83.07	9.36; 9.09	9.33	37.5

In an alkaline medium the decomposition of 1-hydroalkylphosphonic acids probably proceeds further [3]. The organic acids were determined by titration with alkali after they had been liberated from their salts with sulfuric acid and separated from the other hydrolysis products by distillation.

EXPERIMENTAL

Action of Acetyl Chloride on Diethyl 1-Hydroxybutylphosphonate

Acetyl chloride (6.4 g, i.e. 0.081 mole) was added from a dropping funnel to a stirred mixture of 17 g (0.081 mole) of diethyl 1-hydroxybutylphosphonate (b.p. 141-142° (3 mm)), 8.2 g (0.081 mole) of triethylamine, and 150 ml of gasoline (b.p. 70-120°). The reaction mixture was maintained at 65-70° for one hour. After separation of triethylamine hydrochloride and removal of solvent under reduced pressure, the residue, amounting to 20.4 g (100%), was distilled from an Arbuzov flask at a residual pressure of 3 mm. The fractions obtained were:

Fraction I, b.p. 110-117°; 1.5 g
Fraction II, b.p. 117-120°; 18 g

Redistillation of Fraction II gave 10.4 g (50.9%) of a substance having b. p. 111-112° (2 mm); n_D^{20} 1.4312; d_4^{20} 1.0649; found MR 61.28; calculated for $C_{10}H_{21}PO_5$ MR 60.9.

Found %: P 12.53, 12.51. $C_{10}H_{21}PO_5$. Calculated %: P 12.30.

Determination of the Acetyl Group. A solution of a 0.5346-g sample of the sample of the substance in 15 ml of 10% caustic soda was boiled for one hour. The mixture was acidified with sulfuric acid, and solvent was distilled off until an almost dry residue was obtained. Water was added to the residue, and the mixture was again distilled, and the whole of this operation was repeated. The distillates were titrated with alkali.

Acetyl content found 17.21% . $C_{10}H_{21}PO_5$. Acetyl content calculated : 17.06%.

Diethyl 1-acetoxybutylphosphonate is a colorless mobile liquid of feeble odor; it is soluble in organic solvents. Compounds No. 1, 3, and 4 were prepared similarly.

Action of the Mixed Anhydride of Diethyl Hydrogen Phosphite and Acetic Acid on Butyraldehyde

A mixture of 8.77 g (0.034 mole) of tetraethyl pyrophosphite and 2.04 g (0.034 mole) of acetic acid was heated for ten minutes at 110-115°. The mixed anhydride of diethyl hydrogen phosphite and acetic acid so obtained [1] was mixed with 2.45 g (0.034 mole) of butyraldehyde, and the mixture was heated for 45 minutes at 130-140°. Distillation at 4 mm from an Arbuzov flask gave the fractions:

Fraction I, b.p. 47-80°; 4.5 g
Fraction II, b.p. 80-137°; 6 g
Residue 1.5 g

Redistillation of Fraction II gave 2.2 g (25.6%) of a substance having b.p. 123-125° (5 mm); n_D^{20} 1.4318; d_4^{20} 1.0672; found MR 61.23; calculated for $C_{10}H_{21}PO_5$ MR 60.9.

Found %: P 12.68, 12.64. $C_{10}H_{21}PO_5$. Calculated %: P 12.3.

Acetyl content found: 17.29%. $C_{10}H_{21}PO_5$. Acetyl content calculated: 17.06%.

Action of Isobutyryl Chloride on Diethyl α-Hydroxyfurfurylphosphonate

Several drops of a saturated solution of sodium methoxide in methanol were added to a mixture of 13.8 g (0.1 mole) of diethyl hydrogen phosphite and 9.6 g (0.1 mole) of 2-furaldehyde [2]. The temperature of the mixture then rose to 73°. The mixture was heated for one hour at 95-100° and then cooled.

The resulting crude diethyl α-hydroxyfurfurylphosphonate was dissolved in 150 ml of gasoline (b.p. 70-125°), and 10.1 g (0.1 mole) of triethylamine was stirred in. Isobutyryl chloride (10.65 g, i.e. 0.1 mole) was then added from a dropping funnel to the stirred mixture. The temperature was maintained at 65-70° for one hour. After separation of triethylamine hydrochloride and removal of solvent under reduced pressure, the residue, which amounted to 28 g (93.3%), was distilled at 1 mm. The following fractions were obtained:

Fraction I, to 143°; 1.5 g
Fraction II, b.p. 143-147°; 22.6 g

Redistillation of Fraction II gave 20.1 g (67%) of a substance having b.p. 150-151° (1.5 mm); n_D^{20} 1.4637; d_4^{20} 1.1383; found MR 73.62; calculated for $C_{13}H_{21}O_6P$ MR 73.83.

Found %: P 10.36, 10.07. $C_{13}H_{21}O_6P$. Calculated %: P 10.2.

The substance was an odorless viscous yellow liquid, readily soluble in organic solvents, but sparingly soluble in water. Compounds No. 5 and 7 were prepared similarly.

SUMMARY

1. By the action of acetyl, butyryl, and isobutyryl chlorides on some 1-hydroxyalkylphosphonic esters having a hydrogen on the 1-carbon, the corresponding acyl derivatives of the esters were obtained. Some of their physical constants were determined.

2. It was shown that similar compounds can be prepared by reaction of aldehydes with esters of mixed anhydrides of phosphorous acid and various carboxylic acids.

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MECHANISM OF REACTIONS BETWEEN DIAZO COMPOUNDS AND METALS WITH FORMATION OF ORGANOMETALLIC COMPOUNDS*

O. A. Reutov

In 1929 Nesmeyanov [1] discovered the diazo method of synthesizing organometallic compounds, which consists in the decomposition of double diazonium salts with metal powders:

$$ArN_2X \cdot MeX_n \xrightarrow{Me'} Ar_mMeX_{p-m} \text{ or } Ar_nMe'X_{q-n}$$

(p and q are the valencies of metals Meand Me'). The Nesmeyanov reaction has been applied in the synthesis of organic compounds of mercury [2-6], tin [7,8], lead [9,10], arsenic [11-13], antimony [14-22], bismuth [23], and thallium [24].

It has been generally ackowledged that the Nesmeyanov reaction is a homolytic process, proceeding through the stage of neutral radicals. This view, which receives its support mainly from the investigations of Waters [25], is based on the fact that the Nesmeyanov reaction is accompanied by the formation of byproducts which could arise only from the reactions of the neutral radicals Ar· and Cl· (hydrocarbons ArH and products of the chlorination of solvents). Such products, however, could arise in side reactions, whereas the main reaction, in which the organometallic compound is formed, might be heterolytic.

Markovskaya [26] showed that, under the conditions of the Nesmeyanov reaction, double diazonium salts can dissociate with formation of free arenediazonium chloride. The decomposition of the arenediazonium chloride (under the action of the metal, or thermally) naturally results in the formation of free radicals, which react with the solvent. This side reaction, however, is unlikely to have any direct bearing on the reaction between the double diazonium salt and the metal, which results in the formation of an organometallic compound.

We investigated [27] the relation between the rate of the reaction

$$p\text{-}XC_6H_4SbCl_4 \cdot C_6H_5N_2Cl + Fe \rightarrow XC_6H_4(C_6H_5)SbCl_2 + N_2 + FeCl_2$$

and the character of the substitutent X.

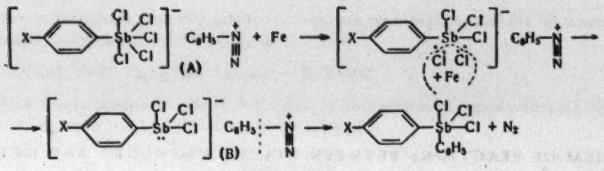
It was found that, with respect to increasing reaction rate, substitutents X fall in the same order as they do with respect to increasing electron-donating power:

$$O_2N < Cl < H < CH_3 < C_2H_5O$$

As electron density is not a determining factor in radical reactions (see, for example, [28]), such a simple relation between reaction rate and the electronegative properties of the substituent is incomprehensible if the reaction is homolytic.

On the other hand, the observed relation can be explained on the assumption that the decomposition of the double salts by, for example, iron prowder is heterolytic in character and may proceed as follows:

* Communication from A. N. Nesmeyanov's department.



It is clear that the heterolytic decomposition of the intermediately formed double salt B (addition of $C_6H_5^+$ at the free electron pair of the antimony atom) will be facilitated by substituents of the first kind and rendered more difficult by substituents of the second kind.

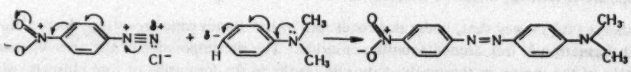
The relation found between the rates of decomposition of the salts $C_6H_5SbCl_4 \cdot p\text{-}YC_6H_4N_2Cl$ and the character of the substituent Y [26] is again in accord (see below) with the hypothesis of a heterolytic mechanism for the reaction (with increase in the electron-donating powers of the substituents, the reaction rate falls:

$$H > CH_3 > C_2H_5O^*).$$

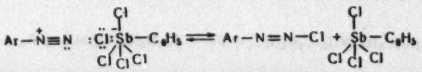
* When Y is a substituent of the second kind (NO_2, $COOC_2H_5$), the double diazonium salt is appreciably dissociated in acetone solution and iron powder brings about two reactions: decomposition of double salt and decomposition of free arenediazonium.

A parallel may be drawn between the tendency of the double salts $C_6H_5SbCl_4 \cdot p\text{-}YC_6H_4N_2Cl$ (and probably also any of the double salts $MCl_n \cdot p\text{-}YC_6H_4N_2Cl$) (Y is a substituent of the second kind) to undergo ready dissociation and the tendency of the diazo compounds $p\text{-}YC_6H_4-\overset{+}{N}\equiv NCl^-$ (Y is a substituent of the second kind) to enter readily into the azo-coupling reaction. The causes of the two phenomena are probably analogous.

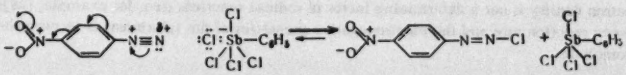
As is well known, p-nitrobenzenediazonium chloride, for example, readily undergoes azo-coupling because the nitro group in attracting electrons creates a partial positive charge on the end nitrogen of the diazo group:



Reversible dissociation, to which all double diazonium salts are to some extent prone, is to a certain extent analogous to the reaction of azo-coupling, for example:



In both reactions the diazonium cation becomes covalently bound with an atom (carbon in the first case and chlorine in the second) by the acceptance of an electron pair. It is clear that the dissociation of a double salt, which consists essentially in the removal of a chlorine anion from an antimony atom by means of a diazonium cation, must resemble azo coupling in being facilitated by substituents of the second kind:



These considerations enable us to understand why 2,4-dinitrobenzenediazonium chloride – one of the most energetic azo-coupling reactants – is quite unable to form double diazonium salts.

Similar conclusions follow from a study of the stability of double diazonium salts of the type $ArSbCl_3 \cdot Ar'N_2Cl$*, which are generally readily decomposed in acetone or ethyl acetate according to the equation:

$$ArSbCl_3 \cdot Ar'N_2Cl \rightarrow ArAr'SbCl_3 + N_2$$

The table lists double diazonium salts of arylantimony dichlorides, which were prepared by the reaction:

$$ArSbCl_2 + Ar'N_2Cl \cdot FeCl_3 \rightarrow ArSbCl_2 \cdot Ar'N_2Cl + FeCl_3.$$

As will be seen from the table, salts of the type $ArSBCl_2 \cdot Ar'N_2Cl$ vary in stability according to the identities of Ar' and Ar [29]. Substituents of the first kind lower the stability of the double salt when they are in the radical of the organoantimony component and raise it when in the radical of the diazo component. On the other hand, substituents of the second kind raise the stability of the double salt when they are in the radical of the organoantimony component and lower it when in the radical of the diazo component.

TABLE

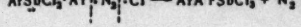
Relation of the Stability of the Double Salt X—C$_6$H$_4$—$SbCl_2 \cdot Y$—C$_6$H$_4$—N_2Cl to the Characters of X and Y

No.	Substituent Y	Substituent X**			
		p-O$_2$N—	p-H$_2$NO$_2$S—	p-H—	p-CH$_3$—
1	p-O$_2$N—	—	—	—	—
2	m-O$_2$N—	—	—	—	—
3	p-C$_2$H$_5$OOC—	—	—	—	—
4	p-CH$_3$—C(=O)—	+	—	—	—
5	p-H—	+	+	+	—
6	p-CH$_3$—	+		+	+
7	p-CH$_3$O—	+		+	+
8	p-C$_2$H$_5$O—		+	+	
9	p-(CH$_3$)$_2$N—	+	+	+	+

** The sign + denotes that a double salt is obtained, and the sign − that the salt cannot exist (decomposes). When no sign appears, the corresponding salt was not investigated.

* In the scheme given above it is assumed that double salts of this type (B) are formed as intermediate compounds.

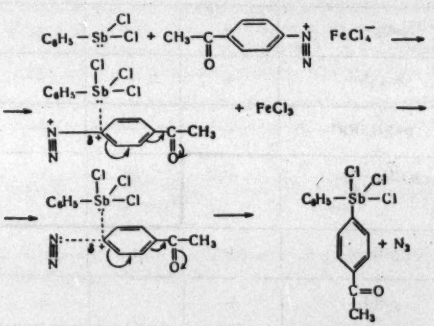
Many salts, particularly those containing a substituent of the second kind in the radical of the diazo component and a substituent of the first kind in the radical of the organoantimony component, are unable to exist, and in all attempts to prepare them they immediately decompose with formation of a diarylantimony trichloride. It does not appear that this phenomenon can be explained on the basis of the view generally held at present, according to which the decomposition of double diazonium salts is a radical reaction:



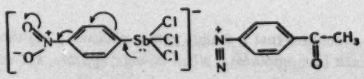
If, however, we suppose that it is a heterolytic reaction:

then the dependence of the stability of the salt $ArSbCl_2 \cdot Ar'N_2Cl$ on the characters of Ar and Ar' can be explained.

The instability of double diazonium salts having substituents of the second kind in the radical of the diazo component is probably due to interaction between the anion of the organoantimony compound and the arenediazonium cation, and this interaction, in its turn, is the result of the presence of a free electron pair on the antimony atom, on the one hand, and a partial positive charge on the carbon atom of the benzene ring attached to nitrogen (due to attraction of electrons by a substituent of the second kind), on the other. For example:



The introduction of a substituent of the second kind into the ortho or para position of phenylantimony dichloride should result in the displacement of the free electron pair of the antimony atom in the direction of the benzene ring, so that the interaction of the antimony atom with the carbon atom of the diazonium radical will be reduced, and the stability of the double salt consequently increased. This is probably the explanation of the ability of p-nitrophenylantimony dichloride to form stable double salts with arenediazonium halides even when the latter contains a substituent of the second kind (acetyl):



In the light of the data considered above we are compelled to reexamine the now generally accepted view of the homolytic character of the synthesis of organometallic compounds via double diazonium salts (particularly the Nesmeyanov reaction) and to advance the hypothesis that these reactions have a heterolytic character.

In conclusion, we shall consider the relationship between the Nesmeyanov reaction and the Waters reaction. According to Waters [25], in the reduction of the double diazonium salt in the course of the Nesmeyanov reaction, free metal is formed and reacts with the arenediazonium halide by the radical mechanism, for example:

$$ArN_2Cl \cdot HgCl_2 + 2Cu \longrightarrow ArN_2Cl + Hg + CuCl_2$$

$$Ar\dot{N}_2 + Cl + \cdot Hg \cdot \longrightarrow Ar-Hg-Cl + N_2$$

This hypothesis, however, is not in accord with various facts.

1) In the decomposition of the double salt $C_6H_5N_2Cl \cdot HgCl_2$ by silver powder, phenylmercury chloride is formed [30], as in the case of decomposition by copper powder:

$$C_6H_5N_2Cl \cdot HgCl_2 + 2Ag \rightarrow C_6H_5 - HgCl + 2AgCl + N_2.$$

In this case, however, the reaction certainly cannot pass through the stage of free-mercury formation, for silver cannot displace mercury from mercuric chloride. The completely analogous decompositions of the double salts

$$(ArN_2Cl)_n \cdot SnCl_4,\ (ArN_2Cl)_n \cdot PbCl_4,\ (ArN_2Cl)_n \cdot PbCl_2 + ArN_2Cl \cdot SbCl_3$$

by copper powder cannot pass through the stage of free-metal formation, though they yield organo-tin, -lead, and -antimony compounds, respectively.

2) If the Nesmeyanov reaction passes through the stage of the formation of free metal, then its field of application should not differ from that of the Waters reaction. However, some organometallic compounds, for example those of bismuth, thallium, and lead, can be prepared only by the first reaction.

3) Finally, the reactions covered by the hypothesis of the intermediate formation of free metal do not include decomposition by metal powders of double salts of the type

$$ArSbCl_4 \cdot ArN_2Cl,\ Ar_2SbCl \cdot ArN_2Cl,\ ArSbCl_4 \cdot ArN_2Cl \rightleftarrows Ar_2SbCl_3 \cdot ArN_2Cl,$$

which results in the formation of new carbon-metal linkages. The intermediate formation of free metal is here excluded entirely, although these reactions are completely analogous, with respect to character and conditions, to the decomposition reactions of double salts of the type $ArN_2Cl \cdot MeCl)_n$.

On the other hand, if we assume that the Waters reaction proceeds, completely or predominantly, through the stage of intermediate formation of double diazonium salts of the metal chlorides:

$$n\,ArN_2Cl + Me \rightarrow n\,Ar\cdot + n\,N_2 + MeCl_n$$

$$ArN_2Cl + MeCl_n \rightarrow ArN_2^+ [MeCl_{n+1}]^-$$
$$\downarrow Me$$
$$Ar - MeCl_{n-1}$$

then the characteristic features of the two reactions (Nesmeyanov and Waters) – which have hitherto been obscure – can be readily understood.

1) It becomes clear why the formation of $ArHgCl$ from ArN_2Cl and Hg will proceed, as McClure and Lowry showed [31], in an aqueous medium, whereas organoantimony and organoarsenic compounds are not formed under these conditions. The reason for this lies in the fact that the $SbCl_3$ and $AsCl_3$ formed by reaction of ArN_2Cl with Sb and As, respectively, are hydrolyzed by water and cannot give the double diazonium salts $ArN_2Cl \cdot SbCl_3$ and $ArN_2Cl \cdot AsCl_3$. In the reaction of ArN_2Cl with mercury, however, the mercuric chloride formed is not hydrolyzed and can give the double salt $ArN_2Cl \cdot HgCl_2$. As it is known that the reaction

$$ArN_2Cl \cdot HgCl_2 + Cu \rightarrow Ar - HgCl + N_2 + CuCl_2$$

can occur in an aqueous medium [32], it is natural to suppose that the decomposition of $ArN_2Cl \cdot HgCl_2$ by finely divided mercury in an aqueous medium will also lead to the formation of ArHgCl:

$$ArN_2Cl \cdot HgCl_2 \xrightarrow[(H_2O)]{Hg} Ar-HgCl$$

Experiments carried out in collaboration with Yu. G. Bundel confirm this view.*

2) One can imagine why the Waters reaction, unlike the Nesmeyanov reaction, does not give organic compounds of bismuth and thallium. The cause probably lies in the fact that the reaction of ArN_2Cl does not go in the cold. At a raised temperature the equilibrium

$$ArN_2Cl \cdot MeCl_3 \rightleftarrows ArN_2Cl + MeCl_3,$$

may be greatly displaced to the right, and the metal will bring about not the decomposition of the double diazonium salt, but the decomposition of the free arenediazonium halide, which does not yield an organometallic compound in the case of these metals.

It is not surprising also that, although ArN_2Cl reacts slowly with Pb in the cold, organolead compounds are not formed in the cold by the Waters reaction, for only very slight yields of organolead compounds are obtained from the double salts $(C_6H_5N_2Cl)_2 \cdot PbCl_2$ and $C_6H_5N_2Cl \cdot PbCl_2$ by the Nesmeyanov reaction.

3) When double diazonium salts of zinc chloride are used instead of free diazonium salts for the synthesis of organoantimony compounds [33], the reaction appears to go according to the scheme:

a) $3(C_6H_5N_2Cl)_2 \cdot ZnCl_2 \xrightarrow{2Sb} 2SbCl_3 + 6C_6H_5\cdot + 3N_2 + 3ZnCl_2$,

b) $(C_6H_5N_2Cl)_2 \cdot ZnCl_2 + 2SbCl_3 \rightleftarrows 2C_6H_5N_2Cl \cdot SbCl_3 + ZnCl_2$,

c) $C_6H_5N_2Cl \cdot SbCl_3 \xrightarrow{Sb}$ organoantimony compounds.

If the formation of organoantimony compounds by the action of antimony on the double diazonium salt of zinc chloride does proceed through the intermediate formation of the double diazonium salt of antimony trichloride $C_6H_5N_2Cl \cdot SbCl_3$, then it is clear that the decomposition of $C_6H_5N_2Cl \cdot SbCl_3$ by antimony under the same conditions should give a higher yield of organoantimony compounds.

Makin and Waters [33] state that in the decomposition of $(C_6H_5N_2Cl)_2 \cdot ZnCl_2$ organoantimony compounds are formed in 26% yield (on the amount of amine taken), whereas in the decomposition of $C_6H_5N_2Cl \cdot SbCl_3$ the yield is only 11%. These results are in conflict with our hypothesis. A repetition of Makin and Waters' experiments showed, however, that they separated only a part of the organoantimony compounds formed in the reaction (namely, triarylantimony dichloride) and therefore gave values that did not correspond to the total yield of organoantimony compounds. Actually, $(C_6H_5N_2Cl)_2 \cdot ZnCl_2$ gives organoantimony compounds in 36% yield, and $C_6H_5N_2Cl \cdot SbCl_3$ gives them in 46% yield.

These results are in accord with the above reaction scheme. It can be understood also why the addition of excess of zinc chloride to the reaction mixture in our experiments was found to reduce the yield of organoantimony compounds.

Returning to the Nesmeyanov reaction, we may point out that the dissociation of the double diazonium salt

$$ArN_2Cl \cdot MeCl_n \rightleftarrows ArN_2Cl + MeCl_n$$

* McClure and Lowry's reaction can be represented as a chain reaction, as follows:

$$2ArN_2Cl + Hg \rightarrow HgCl_2 + 2Ar\cdot + 2N_2;$$
$$ArN_2Cl + HgCl_2 \rightarrow ArN_2Cl \cdot HgCl_2;$$
$$ArN_2Cl \cdot HgCl_2 + Hg \rightarrow Ar-HgCl + N_2 + HgCl_2 \text{ etc.}$$

with formation of free arenediazonium chloride – which increases with rise in temperature – should lower the yield of organometallic compound. It is clear, therefore, why the optimum conditions for most Nesmeyanov reactions are obtained when the decomposition of the double salt is carried out under cooling. An exception is found in the synthesis of organoantimony compounds, which is carried out at about 75° (the total yield of organoantimony compounds attains 80%), but in the decomposition of $ArN_2Cl \cdot SbCl_3$ at 0° with iron powder, still higher yields of organoantimony compounds are obtained [21]. As a substituent of the second kind increases the degree of dissociation of double diazonium salts $XC_6H_4N_2Cl \cdot MeCl_n$, the synthesis of organomercury compounds $XC_6H_4 - HgCl$ (in which X = NO_2, SO_3H, COOH, etc.) requires the use of cooling to a temperature of from −10° to −70° [4] in order to depress this dissociation.

Finally, it must be pointed out that the view that the Waters reaction proceeds through the stage of the formation of double diazonium salts can apply only to metals (Hg, Sb, Sn, etc.). For nonmetals (S, Se, Te), whose chlorides do not give stable double salts with arenediazonium chlorides, the mechanism of reaction with ArN_2Cl will doubtless be different, namely the radical mechanism. There must also be some borderline elements, which can form heteroorganic compounds with ArN_2Cl reacting via two different routes simultaneously: a) by the free-radical reaction of ArN_2Cl with the element, E, and b) by the heterolytic reaction of the element E with intermediate formation of the salt $ArN_2Cl \cdot ECl_n$. It is possible that an example of such a borderline element may be arsenic, whose chloride gives only unstable double salts with ArN_2Cl.

SUMMARY

1. The decomposition of double salts of diazonium and metal chlorides by means of metal powders with formation of organometallic compounds (the Nesmeyanov reaction) is heterolytic in character.

2. The synthesis of organometallic compounds by reaction of arenediazonium chlorides with metal powders (the Waters reaction) proceeds through intermediate formation of a double salt of diazonium and metal chlorides.

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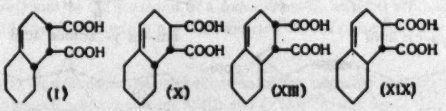
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 12. STEREOCHEMISTRY OF LACTONES OF 1,2,3,5,6,7,8,8a-OCTAHYDRO-1,2-NAPHTHALENEDICARBOXYLIC ACIDS

I. N. Nazarov, V. F. Kucherov and V. M. Andreev

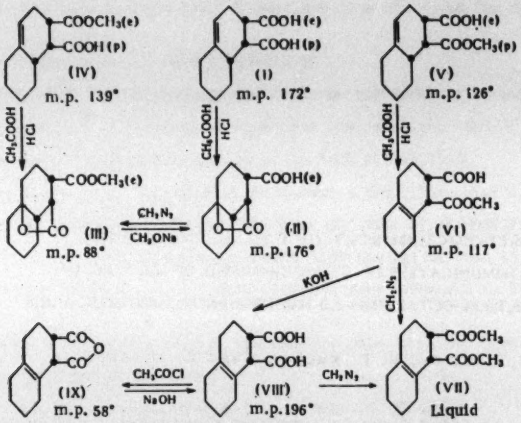
It has already been established [1] that the lactonization of unsaturated cyclic o-dicarboxylic acids is greatly dependent on the steric configuration of these compounds and that the reaction is of great interest for the study of the stereochemistry of cyclic compounds. We have therefore made a detailed study of the lactonization of the four isomeric 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (I), (X), (XIII), and (XIX) described in previous papers [2]. As we had the isomeric monoesters corresponding to the acids (I) and (XIII) at our disposal, we were able not only to prove the structures of the lactones formed, but also to establish their precise steric configurations.



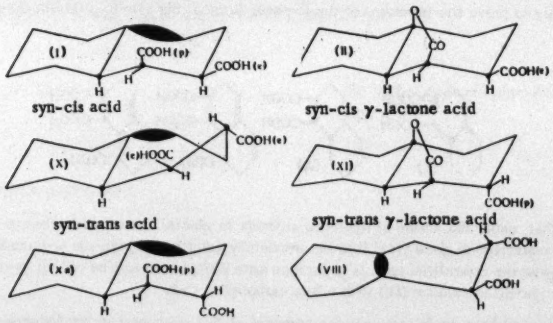
It was found that, under the action of hydrogen chloride in glacial acetic acids, the syn-cis dicarboxylic acid (I) was readily converted in good yield into the previously described [3] syn-cis γ-lactone acid (II). With diazomethane this gave the crystalline syn-cis γ-lactone ester (III), which can be readily prepared also by the lactonization of the syn-cis monoester (IV) with a free carboxyl at C-1.

These data prove without doubt that only the carboxyl at C-1 takes part in the formation of a lactone from the syn-cis acid (I), so that the syn-cis γ-lactone acid (II) obtained must have a γ-lactone structure. The syn-cis γ-lactone ester (III), in which the carboxyl at C-2 is disposed equatorially, was found to be incapable of undergoing isomerization with sodium methoxide; under these conditions it is merely hydrolyzed into the original syn-cis γ-lactone acid (II).

As was to be expected, the isomeric syn-cis monoester (V) having an esterified carboxyl at C-1 was found to be quite incapable of undergoing lactonization; when treated with hydrogen chloride in acetic acid, it was merely isomerized with displacement of the double bond into the intercycle position, as we have noted previously in other similar cases [1]. The new monoester (VI) formed in this way gives the diester (VII) with diazomethane and can be hydrolyzed to the cis-dicarboxylic acid (VIII), which is converted into the cis anhydride (IX) when boiled with acetyl chloride. The fact that the cis acid (VIII) is not hydrogenated in presence of a platinum catalyst under normal conditions shows that it has the structure 1,2,3,4,5,6,7,8-octahydro-1,2-naphthalenedicarboxylic acid, the double bond being between the rings.



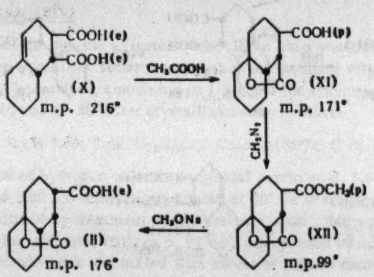
In the above scheme (e) denotes an equatorial disposition of the substituent, and (p) denotes a polar disposition.



The spatial configuration of syn-cis acid (I) is such that the only carboxyl that can take part in lactonization is the polar carboxyl at C-1, which is directed toward the double bond; the product is the syn-cis γ-lactone acid (II), in which the equatorial position of the carboxyl at C-2 is preserved, so that the corresponding syn-cis γ-lactone ester (III) is incapable of isomerization under the influence of sodium methoxide. For the same reason, the isomeric syn-cis monoester (V) having an esterified carboxyl at C-1 cannot undergo lactonization, with the result that the double bond is displaced into the intercycle position with formation of the dicarboxylic acid (VIII). Owing to its flatter structure, this substance is also incapable of lactonization, the carboxyls being considerably removed from the intercycle double bond.

In accordance with the molecular models, the syn-trans acid (X) having a diequatorial (e–e) arrangement of carboxyls is more difficult to lactonize than the isomeric syn-cis acid (I): it gives the syn-trans γ-lactone acid (XI) having a polar carboxyl at C-2 in a yield of only about 40%. As the models show, the lactonization of the syn-trans acid (X) can again occur only at the 1-carboxyl, but in this case the reaction is accompanied by

bending of the cyclohexane ring and corresponds to the lactonization of the unstable form of the syn-trans acid (Xa) having a dipolar (p− p) arrangement of carboxyls. It is very probable that it is this fact that explains the difficult lactonization of the syn-trans acid (X) referred to above .



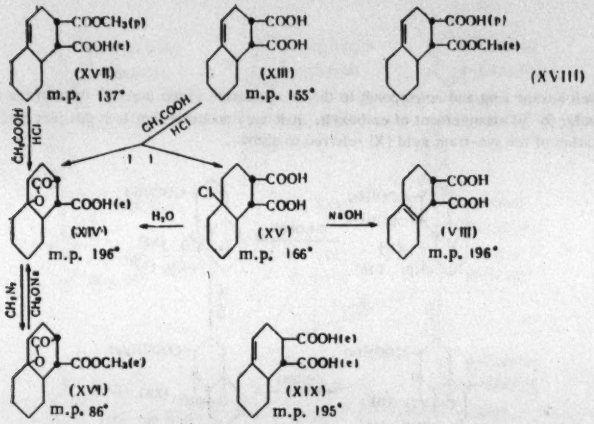
Under the action of diazomethane the syn-trans γ-lactone acid (XI) gives the corresponding lactone ester (XII) having a polar disposition of the methoxycarbonyl group at C-2 so that it is readily isomerized by sodium methoxide into the above-described syn-cis γ-lactone acid (II).

All these results, which support the γ-lactone structure of the syn-cis and syn-trans γ-lactone acids (II) and (XI), were confirmed by infrared-spectrum measurements. The spectra of the γ-lactone esters (III) and (XII), determined in carbon tetrachloride solution, both contained the same two carboxyl bands at 1740 and 1780 cm^{-1}. The first of these bands corresponds to the presence of a free carboxyl, whereas the band at 1780 cm^{-1} indicates that the γ-lactone esters (III) and (XII) contain a γ-lactone ring that is somewhat more highly strained than in simple γ-lactones [4].

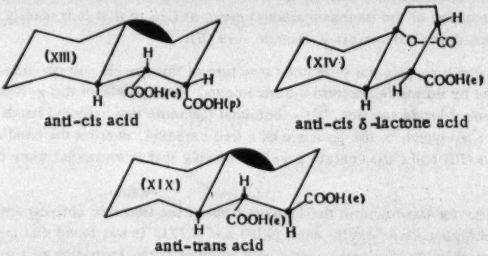
Quite different behavior was found in the lactonization of the isomeric anti-cis and anti-trans 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (XIII) and (XIX). It was found that treatment of the anti-cis acid (XIII) with hydrogen chloride in glacial acetic acid resulted in the formation of a mixture of equal amounts of the anti-cis δ-lactone acid (XIV) and the chlorine-containing dicarboxylic acid (XV), which were readily separated by crystallization.

The chloro dicarboxylic acid (XV), which corresponded in composition to the product of the addition of hydrogen chloride at the double bond, contained mobile chlorine at C-4a: when boiled with water it readily gave the lactone acid (XIV). When hydrolyzed with 5% caustic soda solution, the chloro dicarboxylic acid (XV) was converted in good yield into the above-described unsaturated dicarboxylic acid (VIII) having an intercycle double bond (prepared from the syn-cis monoester (V)). The formation of one and the same dicarboxylic acid (VIII) from the isomeric syn-cis and anti-cis acids (I) and (XIII) confirms previous results [2] showing that these acids are epimers with respect to hydrogen at C-8a, for only in this case can the elimination of a common center of asymmetry lead to a single 1,2,3,4,5,6,7,8-octahydro-1,2-naphthalenedicarboxylic acid (VIII).

On the basis of a study of the chemical reactions of the anti-cis monoester (XVII) and of an examination of the molecular model of the anti-cis acid (XIII) it was found possible to resolve the question of the structure of the anti-cis δ-lactone acid (XIV). It was found that treatment of the monoester (XVII) with hydrogen chloride in glacial acetic acid did not give the possible lactone ester, but gave a good yield of pure anti-cis δ-lactone acid (XIV), converted by diazomethane into the anti-cis δ-lactone ester (XVI), which is not isomerized by sodium methoxide. This shows that, as in the case of the acids (I) and (Xa), in the lactonization of the anti-cis acid (XIII) the polar carboxyl (at C-2) takes part, so that the lactone acid (XIV) must have a δ-lactone ring.



These results are fully in accord with the molecular model of the anti-cis acid (XIII).



As can be seen from the model, in the anti-cis acid (XIII) the equatorial disposition of the carboxyl at C-1 excludes the formation of a γ-lactone, and lactonization can proceed only at the polar carboxyl at C-2 with formation of the anti-cis δ-lactone acid (XIV). In accordance with this, the lactone ester (XVI) has an equatorial methoxycarbonyl group at C-1 and should not therefore be isomerized by sodium methoxide, but the lactonization of the monoester (XVII) should proceed with formation of the lactone acid (XIV) owing to the ready acidolysis of the ester group at C-2.

All these results concerning the δ-lactone structure of the anti-cis lactone acid (XIV) are in accord with facts that we have previously established with regard to the lactonization of anti-cis-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid [1] and were confirmed by a study of the infrared spectrum of the anti-cis δ-lactone ester (XVI). It was found that this lactone ester has a carbonyl absorption band at 1765 cm^{-1} characteristic for δ-lactones; it differs greatly from the absorption band of the γ-lactone esters (III) and (XII). The fact that this band is appreciably displaced toward the shorter waves as compared with simple δ-lactones [4] can be explained by the presence of appreciable strain in the bicyclic δ-lactone acid (XIV), which results in a highly distorted chair form for the B ring.

As indicated by molecular models, the anti-trans acid (XIX) should not be capable of lactonization, owing to the diequatorial (e–e) arrangement of carboxyls. This was confirmed experimentally, for it was found that, when heated with hydrogen chloride in acetic acid, this acid was recovered unchanged in almost quantitative yield.

EXPERIMENTAL

syn-cis γ-Lactone Acid (II)

To 30 ml of a saturated solution of dry hydrogen chloride in glacial acetic acid, 2.7 g of the syn-cis dicarboxylic acid (I), m.p. 172° [2], was added, and the mixture was heated at 60° for one hour. Acetic acid was distilled off under reduced pressure, and the crystalline residue was washed on the filter with ether. Crystallization from 10% aqueous acetone gave 2.2 g of the syn-cis γ-lactone acid (II), m.p. 175-176°, which gave a phenacyl ester of m.p. 132-133° (from 60% alcohol). A lactone acid having the same constants was obtained earlier by Cook and Lawrence [3] by hydrolysis of the maleic anhydride adduct of vinylcyclohexene.

syn-cis γ-Lactone Ester (III)

a) A suspension of 2 g of the syn-cis γ-lactone acid (II) in ether was treated with ethereal diazomethane, ether was distilled off, and the crystalline product was washed on the filter with a mixture of diethyl ether and petroleum ether (1 : 1). The product, amounting to 1.9 g was the syn-cis γ-lactone ester (III), m.p. 82-84°, which melted constantly at 87-88° after crystallization from ether.

Found %: C 65.39, 65.31; H 7.56, 7.49. $C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53.

b) To 5 ml of a solution of hydrogen chloride in glacial acetic acid, 0.5 g of the syn-cis monoester (IV), m.p. 139° [2], was added, and the mixture was heated at 60° for one hour. The residue remaining after removal of solvent was crystallized by treatment with petroleum ether. Recrystallization from diethyl ether gave 0.35 g of the syn-cis γ-lactone ester (III), m.p. 87-88°, undepressed by admixture of the sample prepared as above. When this lactone ester was boiled with excess of sodium methoxide, the original syn-cis γ-lactone acid (II) was recovered almost completely.

cis Monoester (VI)

A mixture of 7.5 g of the syn-cis monoester (V), m.p. 126° [2], and 75 ml of a saturated solution of dry hydrogen chloride in glacial acetic acid was heated at 60° for one hour. Acetic acid was distilled off, and the residue crystallized when vacuum-distilled with benzene and petroleum ether. The product, amounting to 5.4 g was the cis monoester (VI), m.p. 113-116°, raised to 116-117° by recrystallization from a mixture of diethyl ether and petroleum ether.

Found %: C 65.69, 65.80; H 7.84, 7.73. $C_{13}H_{18}O_4$. Calculated %: C 65.51; H 7.53.

cis-Dicarboxylic Acid (VIII)

A mixture of 2.2 g of the cis monoester (VI) and 30 ml of 20% aqueous caustic soda solution was boiled for three hours, filtered, and acidified. The crystalline product was washed on the filter with a little acetone, and 1.9 g of an acid, m.p. 188-190°, was obtained. After crystallization from acetone the pure cis-dicarboxylic acid (VIII) melts at 195-196°, and admixture with the anti-cis δ-lactone acid (XIV) and with the anti-trans dicarboxylic acid (XIX) results in great depression of the melting point.

Found %: C 64.25, 64.20; H 7.27, 7.23. $C_{12}H_{16}O_4$. Calculated %: C 67.27; H 7.19.

Found: M 217.9 (by titration with NaOH)
Calculated: M 224.3.

The acid (VIII) was converted by the usual method into the diphenacyl ester, which melted at 98-99° after crystallization from 85% alcohol.

Found %: C 73.28, 73.23; H 6.24, 6.21. $C_{28}H_{24}O_6$. Calculated %: C 73.02; H 6.13.

cis Anhydride (IX)

A solution of 0.5 g of the cis acid (VIII) in 10 ml of acetyl chloride was boiled for two hours, and volatile substances were then distilled off under reduced pressure. The liquid residue gradually crystallized when allowed to stand with petroleum ether. The product, 0.35 g of cis anhydride (IX), melted constantly at 57-58° after recrystallization from petroleum ether.

Found %: C 69.87, 69.89; H 6.92, 6.88. $C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84.

cis Diester (VII)

The cis monoester (VI) (1.5 g) was treated with ethereal diazomethane. Distillation gave 1.4 g of the cis diester (VII), b.p. 128-129° (2 mm); n_D^{20} 1.4992; d_4^{20} 1.1396; found MR 65.02; calculated MR 65.29.

Found %: C 66.65, 66.63; H 8.06, 7.89; $C_{14}H_{20}O_4$. Calculated %: C 66.65; H 7.99.

The same cis diester (VII) (n_D^{20} 1.4985) was obtained also by the action of diazomethane on the cis-dicarboxylic acid (VIII).

syn-trans γ-Lactone Acid (XI)

A mixture of 2 g of the syn-trans dicarboxylic acid (X) and 30 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. Acetic acid was distilled off, and the liquid residue was dissolved in a small amount of ether and set aside at 0° overnight. The product, amounting to 0.7 g, was the syn-trans γ-lactone acid (XI), m.p. 167-169°, raised to a constant value of 170-171° by recrystallization from water containing a little acetone. The melting point was greatly depressed by admixture of the syn-cis dicarboxylic acid (II).

Found %: C 64.20, 64.14; H 7.28, 7.19. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

Found: M 214.9 (by titration with NaOH)
Calculated: M 224.3.

The lactone acid (XI) was converted by the usual method into the phenacyl ester, which melted at 127-128° after crystallization from 70% ethanol.

Found %: C 70.30, 70.33; H 6.74, 6.59. $C_{20}H_{22}O_5$. Calculated %: C 70.16; H 6.48.

syn-trans γ-Lactone Ester (XII)

A solution of 0.8 g of the syn-trans γ-lactone acid (XV) in ether was treated with excess of diazomethane. Ether was distilled off, and the crystalline product (0.77 g) was recrystallized from petroleum ether. The product, amounting to 0.65 g, was the syn-trans γ-lactone ester (XII), m.p. 98-99°.

Found %: C 65.54, 65.47; H 7.61, 7.64. $C_{13}H_{18}O_4$. Calculated %: C 65.52; H 7.53.

Isomerization of the syn-trans γ-Lactone Ester (XII)

The syn-trans γ-lactone ester (XII) (0.6 g) was added to a solution of 1.4 g of sodium in 50 ml of absolute methanol, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure and the residue was dissolved in 10 ml of water. The solution was filtered, boiled for two hours, and acidified with hydrochloric acid. The oil that separated (0.5 g) gradually solidified, and was found to melt at 145-155°. Two recrystallizations from 20% aqueous acetone gave 0.3 g of the syn-cis γ-lactone acid (II), m.p. 173-174°, undepressed by admixture with the sample described above.

Lactonization of the anti-cis Dicarboxylic Acid (XIII)

A solution of 4 g of the anti-cis dicarboxylic acid (XIII) in 40 ml of acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. Acetic acid was distilled off under reduced pressure, the residue was dissolved in 35 ml of ether, and the solution was set aside overnight. The crystals that separated were filtered off and washed with ether. The product, amounting to 1.8 g, was the anti-cis δ-lactone acid (XIV), m.p. 191-193°, raised to a constant value of 195-196° by recrystallization from a mixture of acetone and ether. Admixture with the cis-dicarboxylic acid (VIII) and with the anti-trans dicarboxylic acid (XIX) resulted in great depression of the melting point.

Found %: C 64.50, 64.34; H 7.37, 7.33. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

Found: M 222.4 (by titration with NaOH)
Calculated: M 224.3.

The phenacyl ester of the lactone acid (XIV) melted at 106-107° after crystallization from 70% ethanol.

Found %: C 70.36, 70.50; H 6.74, 6.64. $C_{20}H_{22}O_5$. Calculated %: C 70.16; H 6.48.

The ethereal solution obtained after the isolation of the lactone acid (XIV) was evaporated, and the liquid residue crystallized out completely when treated with petroleum ether. Two recrystallizations from a mixture of diethyl ether and petroleum ether gave 1.4 g of the pure chloro dicarboxylic acid (XV), melting with decomposition at 165-166°.

Found %: C 55.16, 55.21; H 6.54, 6.65; Cl 13.80, 14.04. $C_{12}H_{11}O_6Cl$. Calculated %: C 55.27; H 6.52; Cl 13.60.

Reactions of the Chloro Dicarboxylic Acid (XV)

a) A solution prepared by dissolving 0.6 g of the chloro acid (XV) in 7 ml of 5% caustic soda solution was boiled until a crystalline precipitate began to form (10 minutes). The crystalline product obtained after acidification (0.4 g) melted at 177-185°. Crystallization from 40% aqueous acetone gave 0.3 g of the cis-dicarboxylic acid (VIII), which melted with decomposition at 194-195°, no depression being shown by admixture of the above-described samples.

b) A mixture of 0.4 g of the chloro acid (XV) and 5 ml of water was boiled for 30 minutes, in the course of which the solution became acid to Congo red. On cooling, an oil separated and rapidly solidified. Washing with 30% aqueous acetone gave 0.25 g of crystals, m.p. 175-185°. One crystallization from acetone-ether mixture gave 0.2 g of the anti-cis δ-lactone acid (XIV), m.p. 193-195°, undepressed by the above-described sample but greatly depressed by admixture with the cis-dicarboxylic acid (VIII) (the mixture melted at 160-170°).

anti-cis δ-Lactone Ester (XVI)

A suspension of 0.5 g of the anti-cis δ-lactone acid (XIV) in ether was treated with excess of diazomethane, and the ether was distilled off. The crystalline product was washed on the filter with a mixture of diethyl ether and petroleum ether (1 : 1). The product, amounting to 0.5 g, was the anti-cis δ-lactone ester (XVI), which had a constant melting point of 85-86° after recrystallization from ether and showed a great depression in admixture with the syn-cis δ-lactone ester (III).

Found %: C 65.56, 65.60; H 7.50, 7.55. $C_{13}H_{16}O_4$. Calculated %: C 65.52; H 7.53.

When an attempt was made to isomerize this lactone ester by boiling it with excess of sodium methoxide, the usual treatment gave only the original anti-cis δ-lactone acid (XIV).

Lactonization of the anti-cis Monoester (XVII)

A solution of 1.5 g of the anti-cis monoester (XVII), m.p. 137° [2], in 20 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for two hours, and acetic acid was distilled off under reduced pressure. The liquid residue partially crystallized out when distilled with petroleum ether. The crystalline product was filtered off and washed with ether. The product, amounting to 0.7 g, was the anti-cis δ-lactone acid (XIV), m.p. 193-194°, undepressed by admixture of the sample prepared previously.

Reaction of the anti-cis Monoester (XVIII) with Hydrogen Chloride in Acetic Acid

A solution of 2 g of the liquid anti-cis monoester (XVIII) [2] in 20 ml of glacial acetic acid saturated with hydrogen chloride was heated at 60° for one hour, and acetic acid was distilled off under reduced pressure. The liquid chlorine-containing reaction product that remained did not crystallize when treated with various solvents and subjected to freezing treatments. As the original anti-cis monoester (XVIII) was not pure and the lactonization reaction was accompanied by the formation of a hydrogen chloride addition product, we did not succeed in isolating the expected anti-cis monoester (XVI). The mixture was hydrolyzed at the boil with 15 ml of 20% aqueous caustic potash. Acidification gave an oil, which crystallized out partly on standing. From this only 0.8 g of the cis-dicarboxylic acid (VIII), m.p. 194-195° with decomposition, could be isolated; it was identical with samples prepared previously (above).

Lactonization of the anti-trans Dicarboxylic Acid (XIX)

A solution of 2 g of the anti-trans dicarboxylic acid (XIX), m.p. 195° [2], in 20 ml of acetic acid saturated with hydrogen chloride was heated at 60° for three hours. Acetic acid was distilled off under reduced pressure, and a crystalline residue remained. Washing on the filter with a little ether gave 1.85 g of

pure original anti-trans dicarboxylic acid (XIX), m.p. 195-196°, greatly depressed by admixture with the anti-cis δ-lactone acid (XIV) and with the cis-dicarboxylic acid (VIII).

SUMMARY

1. A study was made of the dependence of the lactonization reaction on steric structure for all four isomeric 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (I), (X), (XIII), and (XIX).

2. It was shown that the syn-cis dicarboxylic acid (I) and the syn-trans dicarboxylic acid (X) are lactonized to the corresponding isomeric γ-lactone acids (II) and (XI), which contain γ-lactone rings. The acid (X) is lactonized considerably less readily than the isomeric acid (II).

3. Lactonization of the anti-cis dicarboxylic acid (XIII) proceeds with difficulty and gives a mixture of the chloro dicarboxylic acid (XV) and the anti-cis δ-lactone (XIV), the structure of which, as a δ-lactone acid, was confirmed by various chemical reactions and by the infrared spectrum. The anti-trans dicarboxylic acid (XIX) was found to be quite incapable of lactonization.

4. It was shown that, as a result of double-bond displacement, the isomeric syn-cis and anti-cis dicarboxylic acids (I) and (XIII) give the same cis-dicarboxylic acid (VIII), which has an intercycle double bond, this being further confirmation of our previous results on the configurations of the acids (I) and (XIII) as epimers with respect to hydrogen at C-8a.

5. The stereochemical peculiarities of the lactonization of the isomeric, 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids as a function of their spatial configurations were examined and explained with the aid of molecular models.

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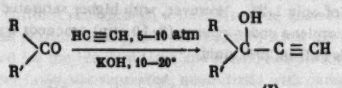
*T.p. = C. B. Translation pagination.

ACETYLENE DERIVATIVES

COMMUNICATION 174. CONDENSATION OF ALDEHYDES AND KETONES WITH ACETYLENE UNDER PRESSURE. II

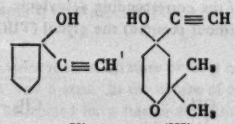
I. N. Nazarov, I. L. Kotlyarevsky and V. F. Ryabchenko

In the preceding communication [1] we described a new method for the synthesis of acetylenic alcohols by the condensation of aldehydes and ketones with acetylene under pressure in presence of caustic potash powder. An important advantage of this method lies in the fact that increase in the pressure of acetylene greatly increases the rate at which it condenses with carbonyl compounds, and it is therefore possible to bring about this reaction rapidly with various aldehydes and ketones and obtain high yields of the corresponding acetylenic alcohols. Under a pressure of 5-10 atm acetylene readily condenses with almost all aliphatic, alicyclic, heterocyclic, aliphatic-aromatic, and aromatic ketones with formation of the corresponding tertiary acetylenic alcohols (I) in 80-95% yield:



(I)

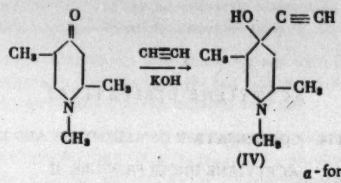
The condensation of acetone, cyclohexanone, and some other simple aliphatic, alicyclic, and heterocyclic ketones with acetylene at a pressure of 5-10 atm in presence of one equivalent of caustic potash is practically complete within 30 minutes of the introduction of the reactants, and the corresponding tertiary acetylenic alcohols are obtained in almost theoretical yields. Higher aliphatic and branched ketones condense more slowly with acetylene and for completion of reaction the reaction mixture must be agitated for 1-3 hours after the introduction of the reactants; tertiary acetylenic alcohols are again obtained in yields of about 90%. Under pressure, acetylene condenses readily also with such alkali-sensitive ketones as cyclopentanone and tetrahydro-2,2-dimethylpyran-4-one, with formation of the corresponding acetylenic alcohols (II) and (III) in yields of about 80%, whereas in absence of pressure these alcohols are obtained in yields of only about 30% [2].



(II) (III)

Aliphatic-aromatic and aromatic ketones, such as acetophenone and benzophenone, condense still more slowly with acetylene, and to carry out this reaction successfully it is necessary to take 2-3 equivalents of caustic potash in order to raise the concentration of potassium acetylide in the reaction mixture. Under these conditions the yields of the corresponding acetylenic alcohols are again above 90%.

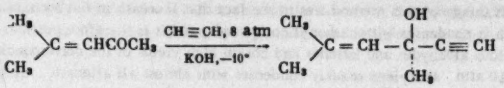
An interesting observation was made in the study of the condensation of acetylene with 1,2,5-trimethyl-4-piperidone. When the acetylene pressure is 1 atm, a 5 : 1 mixture of the α- and β-forms of 4-ethynyl-1,2,5-trimethyl-4-piperidinol (IV) is obtained in an overall yield of 90% [3], whereas at an acetylene pressure of 15 atm the α- and β-forms are obtained in the inverse ratio of 1 : 5.



(IV)

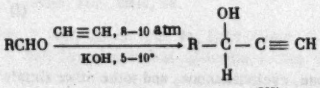
α-form, m.p. 110-111°
β-form, m.p. 177-178°

It is known that α,β-unsaturated aldehydes and ketones are quite unable to condense with acetylene under the usual conditions and that this reaction proceeds satisfactorily only in liquid ammonia or by the use of ethynylmagnesium halides. By the application of pressure (8 atm) we succeeded in effecting the condensation of acetylene with mesityl oxide with formation of the corresponding acetylenic alcohol (V) in 13% yield:



(V)

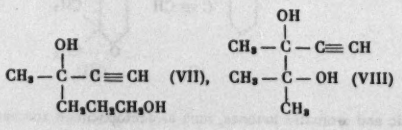
Condensation of acetylene with crotonaldehyde under similar conditions gave the acetylenic alcohol (4-hexen-1-yn-3-ol) in a yield of only 1.2%. However, with higher saturated aldehydes, beginning from propionaldehyde, condensation with acetylene under pressue (8-10 atm) proceeds quite satisfactorily with formation of secondary acetylenic alcohols (VI) in 70% yield:



(VI)

In the condensation of acetylene with acetaldehyde, even under a pressure of 20 atm, 3-butyn-2-ol could not be obtained in yields of greater than 40%, which is to be explained by the high sensitivity of acetaldehyde to alkali and its resinification. For the same reason it was found to be quite impossible to effect the condensation of acetylene with formaldehyde (paraform) in presence of caustic potash. It is known that, in presence of caustic potash powder under the usual conditions (without pressure), aldehydes condense very feebly with acetylene and the method is unsuitable for the preparation of secondary acetylenic alcohols.

Acetylene under pressure condenses readily also with hydroxy ketones (5-hydroxy-2-pentanone, 3-hydroxy-3-methyl-2-butanone) with formation of the corresponding acetylenic glycols (VII) and (VIII) in yields of about 80%, whereas under the usual conditions (without pressure) the glycol (VIII) is obtained in a yield of only about 20%.



In the previous communication it was pointed out that the yield of acetylenic alcohols obtained in the condensation of acetylene with aldehydes and ketones in presence of caustic potash is considerably increased (by 10-15%)

if a little alcohol (0.5-1%; ethyl, butyl, and others) is added to the solvent. This effect is probably to be explained by the action of the aliphatic alcohol as a carrier of potassium ions in the reaction mixture, so that the formation of potassium acetylide is facilitated; its mode of action can be seen from the following equations:

$$CH\equiv CH + KOH \rightleftarrows CH\equiv CK + H_2O$$

$$>CO + CH\equiv CK \rightarrow >C(OK)-C\equiv CH$$

$$>C(OK)-C\equiv CH + ROH \rightleftarrows >C(OH)-C\equiv CH + ROK$$

$$CH\equiv CH + ROK \rightleftarrows CH\equiv CK + ROH \text{ etc.}$$

This also explains the fact that, when less than one equivalent of potassium hydroxide is used in the reaction, the yield of acetylenic alcohol is always higher than would be expected from the simple stoichiometric equation. Thus, in the condensation of acetone with acetylene at 5 atm and 20° in the presence of 8% of ethanol on the weight of acetone and with the use of 1.0, 0.75, and 0.25 equivalent of caustic potash, the respective yields of 2-methyl-3-butyn-2-ol were 92, 80, 71, and 53%. Hence, addition of aliphatic alcohols to the reaction mixture permits the partial regeneration of potassium ions and so increases the yield of acetylenic alcohols.

The described condensation of aldehydes and ketones with acetylene under pressure is the simplest and most general method for the synthesis of the most varied acetylenic alcohols.

EXPERIMENTAL

All the condensations of aldehydes and ketones with acetylene under pressure were carried out in the one-liter and six-liter steel reactors described in the preceding communication [1]. After introduction of solvent and potassium hydroxide powder, air was displaced from the reactor by flushing twice with nitrogen at 5 atm. The stirrer was switched on (400-500 r.p.m.) and acetylene was introduced at the required pressure and temperature. The aldehyde or ketone was then added at a uniform rate through a steel dropping funnel with the aid of a liquid pump. Acetylene was maintained at the required pressure throughout the reaction. After the introduction of the aldehyde or ketone the reaction mixture was stirred for the required time and then treated with water in an amount equal to or double that of the alkali. The upper layer was separated, neutralized with carbon dioxide, dried, and fractionated through a 25-plate column. As solvent in this reaction not only diethyl ether can be used, but also other ethers (including ethers of ethylene glycol), acetals, and various hydrocarbons.

Condensation of Acetylene with Butyraldehyde. A mixture of 50 g of potassium hydroxide powder, 350 ml of ether, and 3 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 55 minutes 65 g of butyraldehyde (b.p. 75-76°) was introduced into the reactor. The reaction mixture was then stirred further for 60 minutes, after which the pressure of acetylene was released and 100 ml of water was introduced into the reactor. The product was extracted with ether, neutralized with carbon dioxide, dried with potassium carbonate, and fractionated. A yield of 64.2 g (72%) of pure 1-hexyn-3-ol (VI: R = n-C_3H_7), b.p. 142-143° and n_D^{20} 1.4350 [4], was obtained.

Condensation of Acetylene with Isobutyraldehyde. A mixture of 760 g of potassium hydroxide powder, 3500 ml of ether, and 30 ml of ethanol was saturated with acetylene at 5° and 6 atm. In the course of two hours 800 g of isobutyraldehyde was introduced into the reactor, and stirring of the reaction mixture continued for a further 50 minutes. The usual treatment gave 720 g (68%) of 4-methyl-1-pentyn-3-ol (VI: R = i-C_3H_7), b.p. 133-134° and n_D^{20} 1.4353 [5].

Condensation of Acetylene with Crotonaldehyde. A mixture of 65 g of potassium hydroxide powder and 350 ml of ether was saturated with acetylene at 0° and 8 atm. In the course of 55 minutes 70 g of crotonaldehyde was introduced into the reactor, and stirring then continued for a further 40 minutes. The usual treatment gave 1.25 g (1.2%) of pure 4-hexen-1-yn-3-ol (VI: R = $CH_3CH{=}CH$) b.p. 57-59° (13 mm) and n_D^{15} 1.4701 [6].

Condensation of Acetylene with 2-Butanone. A mixture of 50 g of potassium hydroxide powder, 300 ml of ether, and 1 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 60 g of 2-butanone was introduced into the reactor. Stirring was then continued for a further 60 minutes. The usual treatment gave 69 g (86%) of 3-methyl-1-pentyn-3-ol (I: R = CH_3, R' = C_2H_5), b.p. 121.5° and n_D^{20} 1.4310 [7]. In

addition, 1.4 g of unchanged 2-butanone was recovered and 1.2 g of the acetylenic γ-glycol was isolated.

Condensation of Acetylene with 3-Pentanone. A mixture of 50 g of potassium hydroxide powder, 300 ml of ether, and 1 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 65 g of 3-pentanone was introduced into the reactor, and stirring was then continued for a further 60 minutes. The usual treatment gave 74 g (90%) of 3-ethyl-1-pentyn-3-ol (I: R = R' = C_2H_5), b.p. 137-138° and n_D^{20} 1.4364 [8]. Also, 2.1 g of unchanged 3-pentanone was recovered and 1.2 g of the acetylenic glycol was isolated.

Condensation of Acetylene with 3-Methyl-2-butanone. A mixture of 100 g of potassium hydroxide powder, 350 ml of ether, and 2 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 120 g of 3-methyl-2-butanone was introduced into the reactor, and stirring was then continued for a further 60 minutes. The usual treatment gave 126 g (82%) of pure 3,4-dimethyl-1-pentyn-3-ol (I: R = CH_3, R' = i-C_3H_7), b.p. 133° and n_D^{15} 1.4590 [9]. Also, 2.6 g of the acetylenic γ-glycol was isolated, and 3.2 g of unchanged 3-methyl-2-butanone was recovered.

Condensation of Acetylene with 2-Pentanone. A mixture of 50 g of potassium hydroxide powder, 300 ml of ether, and 1 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 70 g of 2-pentanone was introduced into the reactor, and stirring was then continued for a further 60 minutes. The usual treatment gave 74 g (84%) of 3-methy-1-hexyn-3-ol (I: R = CH_3, R' = n-C_3H_7), b.p. 138-140° and n_D^{20} 1.4290 [10]. Also, 1.6 g of the acetylenic γ-glycol was isolated and 2 g of unchanged 2-pentanone was recovered.

Condensation of Acetylene with 4-Heptanone. A mixture of 50 g of KOH powder, 300 ml ether and 1 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 60 g of 4-heptanone was introduced into the reactor, and stirring was then continued for a further 60 minutes. The usual treatment gave 63 g (86 %) of 3-propyl-1-hexyn-3-ol (I: R = R' = n-C_3H_7), b.p. 173° and n_D^{20} 1.4375 [11]. Also, 1.5 g of the acetylenic glycol was isolated and 1.6 g of unchanged 4-heptanone was recovered.

Condensation of Acetylene with 2,4-Dimethyl-3-pentanone. A mixture of 50 g of potassium hydroxide powder, 300 ml of ether, and 1.5 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 60 g of 2,4-dimethyl-3-pentanone (b.p. 122-124°) was introduced into the reactor, and stirring was then continued for a further three hours. The usual treatment gave 63 g (86%) of pure 3-isopropyl-4-methyl -1-pentyn-3-ol (I: R = R' = i-C_3H_7), b.p. 165° and n_D^{20} 1.4500 [12]. Also, 2.5 g of the acetylenic γ-glycol was isolated and 2 g of unchanged 2,4-dimethyl-3-pentanone was recovered. It was found that if the period of stirring following the introduction of the 2,4-dimethyl-3-pentanone was 30 or 60 minutes, the yield of the acetylenic alcohol was reduced to 64% or 75%, respectively, and at the same time much of the 2,4-dimethyl-3-pentanone was recovered unchanged. When the condensation of acetylene with 2,4-dimethyl-3-pentanone was carried out at lower pressures (4-5 atm), considerable amounts of the acetylenic γ-glycol were obtained.

Condensation of Acetylene with 2-Octanone. A mixture of 60 g of potassium hydroxide powder, 300 ml of ether, and 1 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 65 g of 2-octanone (b.p. 172-173°) was introduced into the reactor, and stirring was then continued for a further 60 minutes. The usual treatment gave 72 g (92%) of 3-methyl-1-nonyn-3-ol (I: R = CH_3, R' = C_6H_{13}), b.p. 78° (5 mm) and n_D^{20} 1.4408 [13]. In addition, 0.5 g of the acetylenic γ-glycol was obtained.

Condensation of Acetylene with 2-Undecanone. A mixture of 60 g of potassium hydroxide powder, 300 ml of ether, and 1 ml of ethanol was saturated with acetylene at 10° and 10 atm. In the course of 80 minutes 65 g of 2-undecanone (b.p. 221-223°) was introduced into the reactor and stirring was continued for a further 60 minutes. The usual treatment gave 71 g (94%) of 3-methyl-1-dodecyn-3-ol (I: R = CH_3, R' = = C_9H_{19}), b.p. 127-128° (11 mm) and n_D^{20} 1.4474 [14]. Also, 0.8 g of the acetylenic γ-glycol was isolated and 1.1 g of unchanged 2-undecanone was recovered.

Condensation of Acetylene with Mesityl Oxide. A mixture of 98 g of potassium hydroxide powder, 350 ml of ether, and 4 ml of ethanol was saturated with acetylene at −5° and 15 atm. In the course of 45 minutes 95 g of mesityl oxide (b.p. 129-131°) was introduced into the reactor, and stirring of the reaction mixture was then continued for a further two hours. The usual treatment gave 10 g (11%) of 3,5-dimethyl-4-hexen-1-yn-3-ol (V), b.p. 65-66° (17 mm) and n_D^{20} 1.4629 [15], and 58 g of unchanged mesityl oxide was recovered. The residue from the distillation amounted to 29 g. The performance of this condensation at higher pressures of acetylene (up to 25 atm) did not result in appreciable increase in the yield of the acetylenic alcohol (V).

Condensation of Acetylene with 1,2,5-Trimethyl-4-piperidone. A mixture of 75 g of potassium hydroxide powder and 350 ml of dry ether was saturated with acetylene at −8° and 15 atm. In the course of 60 minutes a solution of 100 g of 1,2,5-trimethyl-4-piperidone in 100 ml of ether was introduced into the reactor, and stirring of the reaction mixture was then continued for a further 45 minutes. Treatment as described previously [3] resulted in the isolation of 19.7 g of the low-melting α-form of 4-ethynyl-1,2,5-trimethyl-4-piperidinol (IV), m.p. 110-111°, and 81.5 g of the high-melting β-form, m.p. 177-178°. When this reaction is carried out at an acetylene pressure of 1 atm, then, as shown previously [3], the α- and β-forms of the piperidinol (IV) are formed in the inverse ratio (5 : 1).

Condensation of Acetylene with 2-Methylcyclohexanone. A mixture of 80 g of potassium hydroxide powder, 350 ml of ether, and 1 ml of ethanol was saturated with acetylene at 13° and 10 atm. In the course of 65 minutes 100 g of 2-methylcyclohexanone was introduced into the reactor, and stirring was then continued for a further 60 minutes. The usual treatment gave 111 g (96%) of 1-ethynyl-2-methylcyclohexanol, b.p. 72° (8 mm) and n_D^{20} 1.4720 [16]. Also, 2.1 g of the acetylenic γ-glycol was isolated and 2.8 g of 2-methylcyclohexanone was recovered.

Condensation of Acetylene with Tetrahydro-2,2-dimethylpyran-4-one. A mixture of 120 g of potassium hydroxide powder and 350 ml of ether was saturated with acetylene at 8° and 6 atm. In the course of 60 minutes 100 g of tetrahydro-2,2-dimethylfuran-4-one was introduced into the reactor, and stirring was then continued for a further three hours. The usual treatment gave 96 g (82%) of pure 4-ethynyltetrahydro-2,2-dimethylpyran-4-ol (III), b.p. 77° (3 mm), m.p. 87° [2], and 2.6 g of unchanged tetrahydro-2,2-dimethylfuran-4-one was recovered.

Condensation of Acetylene with cis-Octahydro-2(1H)-naphthalenone. A mixture of 81 g of potassium hydroxide powder and 350 ml of ether was saturated with acetylene at 7° and 5 atm. In the course of 50 minutes 76 g of cis-octahydro-2(1H)-naphthalenone was introduced into the reactor, and stirring was then continued for a further three hours. The usual treatment gave 84 g (94%) of cis-2-ethynyldecahydro-2-naphthol, b.p. 92-93° (3 mm) and n_D^{20} 1.5112 [17], and 1.8 g of unchanged cis-octahydro-2(1H)-naphthalenone was recovered.

Condensation of Acetylene with trans-Octahydro-1(2H)-naphthalenone. A mixture of 80 g of potassium hydroxide powder and 300 ml of ether was saturated with acetylene at 15° and 10 atm. In the course of 90 minutes 90 g of trans-octahydro-1(2H)-naphthalenone was introduced as a solution in 100 ml of ether, and stirring was then continued for a further three hours. The products were 90.5 g (90%) of trans-1-ethynyldecahydro-1-naphthol, b.p. 98-99° (2 mm) and n_D^{20} 1.5060 [18], 1.5 g of the acetylenic γ-glycol, and 4.5 g of unchanged trans-octahydro-1(2H)-naphthalenone.

Condensation of Acetylene with Cyclopentanone. A mixture of 470 g of potassium hydroxide powder, 2500 ml of ether, and 10 ml of ethanol was saturated with acetylene at 10° and 7 atm. In the course of 90 minutes 465 g of cyclopentanone was introduced into the reactor, and stirring was then continued for a further 90 minutes. The usual treatment and fractionation through a column gave 458.5 g of 1-ethynylcyclopentanol (II), b.p. 157° and m.p. 27° [19].

Condensation of Acetylene with 5-Hydroxy-2-pentanone. A mixture of 130 g of potassium hydroxide powder and 350 ml of ether was saturated with acetylene at 5° and 8 atm. In the course of 35 minutes 102 g of 5-hydroxy-2-pentanone, b.p. 102-105° (20 mm) and n_D^{15} 1.4410, was introduced into the reactor, and stirring was then continued for a further two hours. The usual treatment and fractionation gave 65 g (57%) of pure 4-methyl-5-hexyn-1,4-diol (VII), b.p. 110-113° (5 mm) and n_D^{20} 1.4680.

Found %: C 65.48, 65.21; H 9.06, 8.91. $C_7H_{12}O_2$. Calculated %: C 65.52; H 9.25.

In addition, 6.2 g of unchanged 5-hydroxy-2-pentanone was recovered. In the hydrogenation of 10 g of the acetylenic glycol (VII) in 15 ml of methanol in presence of a palladium catalyst, 3620 ml of hydrogen (15°, 755 mm) was absorbed in 2.5 hours instead of 3720 ml, as required theoretically. The product, amounting to 9.2 g, was 4-methylhexane-1,4-diol, b.p. 102° (4 mm) and n_D^{20} 1.4575.

Condensation of Acetylene with 3-Hydroxy-3-methyl-2-butanone. A mixture of 65 g of potassium hydroxide powder, 300 ml of ether, and 1 ml of ethanol was saturated with acetylene at 0° and 10 atm. In the course of 70 minutes a solution of 51 g of 3-hydroxy-3-methyl-2-butanone (b.p. 140-141° [20]) in 50 ml

of ether was introduced into the reactor, and stirring was then continued for a further 60 minutes. The main product, amounting to 50.2 g (84%), was 2,3-dimethyl-4-pentyn-2,3-diol (VIII), b.p. 79-80° (10 mm) and n_D^{20} 1.4640 [21]. Also, 7 g of the acetylenic erythritol was isolated and 8 g of unchanged 3-hydroxy-3-methyl-2-butanone was recovered.

SUMMARY

A further study was made of a new method of synthesizing secondary and tertiary acetylenic alcohols by the condensation of aldehydes and ketones with acetylene under pressure in presence of potassium hydroxide powder.

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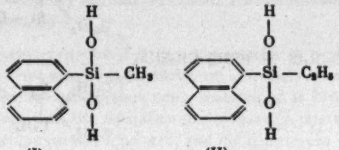
SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 5. SYNTHESIS AND REACTIONS OF ALIPHATIC-AROMATIC SILANEDIOLS

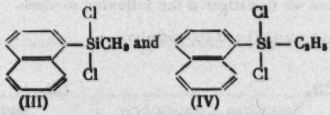
M. F. Shostakovsky and Kh. I. Kondratyev

For the further development of the chemistry of vinyl ethers it is important that their reactions with silanols [1-6] and silanediols should be investigated. Of the organic silanediols, those of the aliphatic-aromatic series are of great interest. In the present paper we describe the synthesis of silanediols of the following structure:



(I) (II)

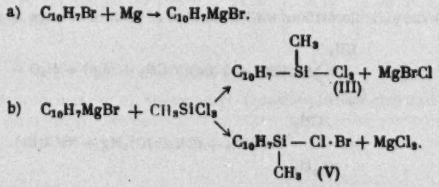
The starting materials for the preparation of the compounds (I) and (II) were the following dichloro compounds:



(III) (IV)

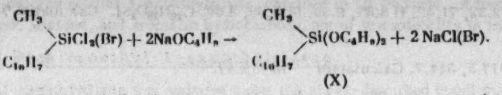
The preparation of (III) was carried out in two ways – via organomagnesium compounds and via organolithium compounds. The dichloro compound (IV) was prepared only by the second method.

The formation of the dichloro compound (III) by the first of these methods proceeded according to the scheme:



c) $2C_{10}H_7MgBr + CH_3SiCl_3 \rightarrow \begin{matrix} C_{10}H_7 \\ C_{10}H_7 \end{matrix}\!\!>\!\!SiCl(Br) + 2MgClBr.$
$\quad\quad\quad

Ethyl-1-naphthylsilanediol was prepared by the hydrolysis of the corresponding dichloro compound with 0.1 N NaOH. The silanediols obtained, (I) and (II), were characterized by their physical constants and elementary analysis. Chlorine and bromine were determined in the mixture of products (III) and (V), and the derivatives (IX) and (X) were prepared in order to prove their structure:



(X)

EXPERIMENTAL

1. Synthesis of Dichloromethyl-1-naphthylsilane by the Organomagnesium Method

a) Preparation of 1-Naphthylmagnesium Bromide. A mixture of 52.8 g of magnesium turnings, 250 ml of absolute ether, and a crystal of iodine was prepared in a flask fitted with reflux condenser, dropping funnel, thermometer, and mechanical stirrer, and air was displaced from the apparatus by a stream of nitrogen. A feeble stream of nitrogen was maintained while 20 g of 1-bromonaphthalene and 2 ml of ethyl bromide were introduced into the flask. When reaction set in, the stirrer was switched on, water cooling was applied, and a mixture of 394 g of 1-bromonaphthalene, 750 ml of ether, and 100 ml of benzene was added at such a rate that reaction occurred with gentle boiling of the ether. The addition required about three hours, and stirring was then continued for a further 40 minutes, when 300 ml of dry benzene was added and the solution of 1-naphthylmagnesium bromide was separated from unchanged magnesium.

b) Preparation of Dichloromethyl-1-naphthylsilane. The solution of 1-naphthylmagnesium bromide was added over a period of 2.5 hours to a solution of 296 g (2 moles) of trichloromethylsilane in 100 ml of benzene under the conditions described above, the temperature being maintained at 20-35°. The mixture was then maintained at a gentle boil and was stirred until the separation of the reaction mixture into two layers ceased (2-3 hours). When the mixture was cool, the precipitate was separated, and the filtrate was vacuum-fractionated. In all, 210 g of a substance of b.p. 161-165° (9 mm) or 183-187° (19 mm) was obtained. This product was crude dichloromethyl-1-naphthylsilane. It was redistilled under reduced pressure, and chlorine and bromine was determined in the resulting fractions by titration of a sample (0.1-0.4 g) with 0.1 N NaOH to phenolphthalein, the sample being added to 20 ml of water and 20 ml of ether contained in a flask. The aqueous layer was then separated and its bromine content determined by the method proposed by Volyashko and others [15]. The results are given in the table.

TABLE

Chlorine and Bromine Contents of Crude Dichloromethyl-1-naphthylsilane

Fraction	B.p. (°C) at 19 mm	Amount (g)	Halogen content (%)		d_{20}^{20}	n_D^{20}
			Cl	Br		
I	183—184	9.0	22.76	2.47		
II	184—185	55.3	24.25	3.50	1.223	1.6018
III	185—186—2	29.8	23.2	5.50	1.252	1.6024
IV	186.2—187	15.9	21.9	7.14	1.286	1.6018
Residue		36.0	20.5	6.10		

From these results it follows that the dichloromethyl-1-naphthylsilane obtained was contaminated with bromine derivative.

2. Preparation of the Dibutyl Ether of Methyl-1-naphthylsilanediol

Over a period of 90 minutes 296 g of dichloromethyl-1-naphthylsilane* was added from a dropping funnel to a well stirred solution of sodium butoxide in xylene (139 g of butyl alcohol, 43 g of sodium, and 600 g of xylene). The mixture was diluted with an equal volume of water, and the xylene layer was separated and fractionated. The product, amounting to 257 g (81.2%), boiled at 195-204° (12.5-15 mm) and corresponded in composition to the dibutyl ether of methyl-1-naphthylsilanediol. It had d^{20} 0.9983 and n_D^{20} 1.5270.

Found %: C 72.32, 71.42; H 8.85, 8.96; Si 8.63, 8.60. $C_{19}H_{28}O_2Si$. Calculated %: C 72.10; H 8.91; Si 8.87.

Found: M 317.5, 314.7. Calculated: M 316.47.

The dibutyl ether of methyl-1-naphthylsilanediol is a colorless liquid which is of good solubility in the usual organic solvents.

3. Preparation of the Diacetic Ester of Methyl-1-naphthylsilanediol

A solution of 0.25 mole of dichloromethyl-1-naphthylsilane in 60 ml of petroleum ether (b.p. 60-75°) was added from a dropping funnel over a period of 40 minutes to a well stirred mixture of 41 g of anhydrous sodium acetate and 90.3 g of petroleum ether at about 40°. Stirring was then continued for a further 45 minutes. The reaction mixture was set aside for 12 hours, and the crystalline precipitate that had formed was then filtered off. Petroleum ether was distilled from the filtrate, and the residue was vacuum-fractionated. The main fraction boiled at 175-179° (12 mm) and had the following analysis:

Found %: CH_3COO 39.60, 39.66; Si 9.5, 9.6. $C_{15}H_{16}O_4Si$. Calculated %: CH_3COO 40.97; Si 9.70.

This corresponds to the diacetic ester of methyl-1-naphthylsilanediol. The diacetic ester of methyl-1-naphthylsilanediol is a clear viscous oil which is soluble in the usual organic solvents. Alkaline hydrolysis converts it into methyl-1-naphthylsilanediol.

4. Preparation of Dichloromethyl-1-naphthylsilane by the Organolithium Method

a) Preparation of a Solution of Butyllithium. Benzene (300 ml) was introduced into the reaction vessel, and air was displaced by dry nitrogen (all operations with lithium were carried out in a nitrogen atmosphere). Lithium (15 g, cut into small pieces) was added, and the mixture was stirred while 102 g of butyl chloride was added from a dropping funnel over a period of 90 minutes at 50-60°. When the whole of the butyl chloride had been added, the reaction mixture was heated for a further 30 minutes. Dry benzene was added to the product, the mixture was cooled to room temperature, and after two hours the butyllithium solution was separated from lithium chloride. The butyllithium content of the filtrate (640 g) was determined by titration with 0.1 N NaOH. It was found to be 50.1 g, corresponding to a yield of 73.3%.

b) Preparation of 1-Naphthyllithium. A solution of 162 g of 1-bromonaphthalene in 100 ml of benzene was added from a dropping funnel over a period of 30 minutes to the butyllithium solution, the temperature being initially 18-20° and finally 40-45°. The precipitate formed, which contained 70.7 g (67.5%) of 1-naphthyllithium, was filtered off.

c) Preparation of Dichloromethyl-1-naphthylsilane. A suspension of 70.7 g of 1-naphthyllithium in 140 ml of benzene was added from a dropping funnel to a constantly stirred solution of 78 ml of trichloromethylsilane in 120 ml of benzene, the temperature of the reaction mixture being maintained at about 40° (water cooling). The reaction mixture was stirred for a further one hour and then fractionated. The product (60.2 g) had b.p. 123-125° (1.5 mm), d_{20}^{20} 1.237; n_D^{20} 1.6028. The literature [16] gives b.p. 122° (1 mm), d_{20}^{20} 1.2333; n_D^{20} 1.6025.

Found %: C 55.62, 55.56; H 4.38, 4.36; Cl 28.35, 28.50; Si 11.60, 11.53. $C_{11}H_{10}Cl_2Si$. Calculated %: C 54.78; H 4.18; Cl 29.41; Si 11.63.

The analysis shows that the isolated product corresponds to dichloromethyl-1-naphthylsilane, which was obtained in 47.4% yield. Dichloromethyl-1-naphthylsilane is a colorless viscous liquid having a sharp suffocating odor. It gradually decomposes in the air with evolution of hydrogen chloride. In appearance and properties it is similar to the dichloromethyl-1-naphthylsilane obtained from $1\text{-}C_{10}H_7MgBr$ and CH_3SiCl_3.

* For the syntheses of the dibutyl ether and diacetic ester of methyl-1-naphthylsilanediol, dichloromethyl-1-naphthylsilane prepared by the organomagnesium method was used.

The residue from the distillation (16.7 g) was crystallized from a mixture of benzene and heptane, and 12 g of crystals melting at 132° were obtained.

Found %: C 76.51, 76.48; H 4.89, 4.79; Cl 10.39, 10.54; Si 8.19, 7.67. $C_{11}H_{17}ClSi$. Calculated %: C 75.77; H 5.15; Cl 10.65; Si 8.43.

This product is chloromethyldi-1-naphthylsilane, obtained in 18.7% yield. It forms colorless crystals, readily soluble in ether, acetone, and aromatic hydrocarbons, but of low solubility in isopentane.

5. Synthesis of Dichloroethyl-1-naphthylsilane

Dichloroethyl-1-naphthylsilane was prepared under the above-described conditions from 161.9 g of 1-naphthyllithium and 196 g of trichloroethylsilane. After removal of solvent the reaction product was vacuum-fractionated. The following fractions were obtained:

Fraction I, b.p. 79-120° (1.5-2 mm);	1.7 g
Fraction II, b.p. 122-134° (1.5-2 mm);	12.43 g (the bulk of this boiled at 132-134°)
Fraction III, b.p. 134-136° (1.5-2 mm);	153 g
Residue	68.38 g

Fraction I was recrystallized from ethanol, and 1.2 g of naphthalene was isolated. Fraction II consisted mainly of contaminated dichloroethyl-1-naphthylsilane. Fraction III was the main product; it had the following constants: d_{20}^{20} 1.222; n_D^{20} 1.5995; the yield was 49.67%.

Found %: C 56.74, 56.50; H 4.83, 4.77; Cl 28.14, 27.74; Si 11.04, 11.17. $C_{12}H_{12}Cl_2Si$. Calculated %: C 56.52; H 4.74; Cl 27.79; Si 11.0.

On the basis of our results, this substance is dichloroethyl-1-naphthylsilane. It is a viscous liquid, readily soluble in the usual organic solvents. The residue (68.38 g of a viscous semisolid mass) was repeatedly recrystallized from heptane, the crystals being washed with isopentane. The crystals, amounting to 49.9 g (23.8%), melted at 94°.

Found %: C 75.86, 75.34; H 5.69, 5.68; Cl 11.14, 11.74. $C_{22}H_{19}ClSi$. Calculated %: C 76.15; H 5.52; Cl 10.22.

The product, chloroethyldi-1-naphthylsilane, is readily soluble in ether, acetone, and aromatic hydrocarbons, but is sparingly soluble in isopentane.

6. Preparation of Methyl-1-naphthylsilanediol

a) Hydrolysis of the Diacetic Ester of Methyl-1-naphthylsilanediol with 0.1 N NaOH. Ether (30 ml), an ampoule containing 1 g of the diacetic ester of methyl-1-naphthylsilanediol, and 20 g of finely crushed ice were introduced successively into a flask, which was then shaken vigorously to break the ampoule. The mixture was titrated with 0.1 N NaOH in presence of phenolphthalein. The aqueous layer was separated from the ether layer and washed with ether. The ether extracts were washed with water, and ether was distilled off at 15-20 mm. The oily residue was dissolved in benzene. After some time, 0.36 g (50.8%) of crystals, m.p. 106-107°, separated from the benzene solution.

Found %: C 65.35, 65.30; H 6.13, 5.99; Si 12.85, 13.02; O 15.67, 15.69. $C_{11}H_{12}O_2Si$. Calculated %: C 64.69; H 5.91; Si 13.74; O 15.67.

Found M 197.3, 195.3. Calculated %: M 204.

Methyl-1-naphthylsilanediol is readily soluble in ether, alcohol, and acetone; it is sparingly soluble in benzene and petroleum ether.

b) Hydrolysis of Dichloromethyl-1-naphthylsilane with Aqueous Sodium Acetate in presence of Magnesium Oxide. A mixture of 0.5 mole of sodium acetate, 0.25 mole of magnesium oxide, 125 g of water, and 125 g of ether was prepared in a flask fitted with reflux condenser, mechanical stirrer, and dropping funnel, and 0.25 mole of dichloromethyl-1-naphthylsilane was added gradually to the mixture from a dropping funnel, the temperature being about 0°. When the hydrolysis was complete, the ether solution was separated from the aqueous layer and dried with sodium sulfate. Part of the ether was removed under reduced pressure, and petroleum ether was added to the residue, which resulted in the separation of a precipitate.

Recrystallization from benzene and petroleum ether gave methyl-1-naphthylsilanediol in the form of glistening crystals, m.p. 106-107°. In admixture with the methyl-1-naphthylsilanediol obtained by the hydrolysis of the diacetic ester of methyl-1-naphthylsilanediol, there was no melting-point depression.

7. Preparation of Ethyl-1-naphthylsilanediol

Hydrolysis of Dichloroethyl-1-naphthylsilane with 0.1 N NaOH. A mixture of 1.1087 g of dichloroethyl-1-naphthylsilane, 25 g of finely crushed ice, and 35 ml of ether was titrated with 0.1 N NaOH in presence of phenolphthalein. The ether layer was separated, ether was distilled off under reduced pressure, and 6 ml of benzene and 20 ml of petroleum ether were added to the residue. The crystals that separated were removed and dried at a residual pressure of 2 mm. The product, amounting to 0.48 g, melted at 89-90°.

Found %: C 66.20, 66.10; H 6.42, 6.63; Si 12.44, 12.43. $C_{12}H_{14}O_2Si$. Calculated %: C 66.04; H 6.46; Si 12.85.

Found: M 226.3, 216.1. Calculated: M 218.29.

The results correspond to ethyl-1-naphthylsilanediol. This substance is readily soluble in ether, alcohol, and acetone, but sparingly soluble in isopentane and benzene.

SUMMARY

1. It was shown that the dichloromethyl-1-naphthylsilane obtained by the organomagnesium method contains bromochloromethyl-1-naphthylsilane as impurity.

2. The procedure for preparing pure arylalkyldichlorosilanes was improved.

3. Conditions were found for the preparation of alkylarylsilanediols in the pure state by the hydrolysis of alkylaryldihalosilanes.

4. The following substances were prepared and characterized for the first time: methyl-1-naphthylsilanediol, ethyl-1-naphthylsilanediol, dichloroethyl-1-naphthylsilane, chloroethyldi-1-naphthylsilane, chloromethyldi-1-naphthylsilane, the dibutyl ether of methyl-1-naphthylsilanediol, and the diacetic ester of methyl-1-naphthylsilanediol.

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KINETICS AND CHEMISTRY OF THE POLYCONDENSATION OF GLYCINE ETHYL ESTER

K. T. Poroshin, T. D. Kozarenko and Yu. I. Khurgin

(Abridged text of a paper read at a general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR held in Moscow, April 25, 1956)

A considerable number of papers have appeared on the polycondensation of esters of α-amino acids [1-8]. The data now available, however, do not give us any idea of the kinetics and chemistry of the reaction and the composition of the polycondensation products. The polycondensation reaction attracts interest for two reasons: in the first place, this reaction, and its mechanism and kinetics, is closely associated with the problem of the synthesis of the peptide link, which is of great importance for biochemistry; and in the second place, as we have already shown, the polycondensation reaction carried out under our conditions [9,10] has a non-equilibrium character and therefore forms a suitable basis for a study of the polycondensation reaction.

The first attempt to determine the composition of the polycondensation product obtained from esters of α-amino acids was made by Curtius [1], who tried to determine quantitatively the piperazinedione formed in the condensation of glycine ethyl ester. The lack of success in this first attempt is to be attributed to the absence of a suitable analytical method. Frankel and Katchalski [3] investigated the polycondensation of alanine esters and used the sublimation method for the determination of piperazinediones. Using the chromatographic method, Brockmann and Musso [5] and Schramm and Restle [6] obtained more detailed information of the composition of the polycondensation product obtained from esters of low oligopeptides. It should be noted, however, that the available data on the composition of polycondensation products obtained from esters of amino acids and of oligopeptides relate to reaction conditions that are selected arbitrarily and are usually severe, the reaction generally proceeding to an advanced stage, so that there is no information about the intermediate stages of the reaction. The present work is the first attempt to make a systematic investigation of the composition of the polycondensation product at various stages of the process. In selecting a substance for investigation, we decided on glycine ethyl ester for the following reasons: 1) the reactions of glycine ethyl ester have been the subject of several investigations and have therefore been studied in the greatest detail; 2) we have previously [9,10] determined conditions for carrying out the polycondensation of glycine ethyl ester which enabled us to obtain unequivocal and reproducible results. The study of the composition of the polycondensation product of glycine ethyl ester at various stages of the process is convenient also because we have previously developed methods for the determination of piperazinedione [11] and diglycylglycine [12] in the products of this reaction. Glycine esters are readily distilled, especially at reduced pressure, and this permits the separation of unchanged monomer from the reaction mixture. This makes it possible to determine the progress of reaction with comparative ease.

The high water-solubility of the glycine peptides formed in the early stages of the polycondensation reaction considerably increases the accuracy with which their composition can be determined by titration with copper in alkaline solution and measurement of amine nitrogen by the van Slyke method. At later stages of the reaction (after 20 hours) macromolecular polyglycine makes its appearance; this is of low solubility in water and weak alkalis, and we therefore limited the duration of the experiment to 15 hours. The most interesting transformations were observed during the first 8-10 hours, after which there occurred only slight quantitative changes associated with the further gradual increase in the molecular weight of the polyglycine.

Tetrapeptides and peptides of still higher molecular weight make their appearance already after 2-3 hours, after which they increase continuously in amount. It is interesting to note that the relative amount of piperazinedione in the polycondensation product of glycine ethyl ester is not constant, but gradually falls as the reaction progresses. At the beginning of the reaction (1.5-2 hours) the amount of piperazinedione attains 40% of the total amount of polycondensation product and then gradually falls to 17-19%. In the early stages of the reaction (5-6 hours) the amount of diglycylglycine ethyl ester rises at first, attains a maximum value (about 30%), and then falls continuously as the rate of its conversion into compounds of higher molecular weight rises relative to the rate of re-formation of the ester of the tripeptide.

A study of the kinetics of the conversion of monomer into the respective condensation products showed that transformation occurs in accordance with a first-order law, the rate constant in presence of carbon dioxide being $5.85 \cdot 10^{-5}$ second^{-1}.

EXPERIMENTAL

Glycine ethyl ester, prepared by Fischer's method [13], was introduced into ampoules together with catalyst (carbon dioxide; 2 moles % on the amount of ester) in the way described previously [9]. All experiments were carried out at 40 ± 0.01°, a temperature at which no degradation of peptides was observed. At the end of the required time (more than two hours) the ampoule was opened and its contents were transferred to a vessel containing absolute ether (10-12 times the volume of the contents of the ampoule) for the extraction of monomer.

The solid mass of polymer was carefully broken down with a glass rod until a fine white suspension was formed. The polycondensation product was filtered off and washed with two or three successive portions of ether. The white powder so obtained was dried for 3-4 hours in a vacuum over concentrated sulfuric acid; it was then investigated.

In order to determine the amount of piperazinedione in these products, a weighed sample (20-30 mg) was dissolved in water (3-5 ml) and a portion of the solution was analyzed for amine nitrogen by the van Slyke method. At the same time, a sample of the solid substance was dissolved in 0.1 N NaOH and heated for two hours at 40° with subsequent determination of amine nitrogen. From the increase in amine nitrogen after hydrolysis of the piperazinedione, the amount of this in the solid phase was determined (Curve 1, Fig. 1) and was recalculated for all the products in the reaction medium (i.e. on the weight of monomer taken) to give the percentage of piperazinedione on the total weight of reaction mixture (Curve 1, Fig. 2).

It should be noted that, at the beginning of the process (after about two hours), about one-half of the solid part of the polycondensate is piperazinedione. It may be assumed that at still earlier stages of the reaction the amount of piperazinedione will be still greater, but the amount of polycondensate formed in these stages is too small for the accurate determination of piperazinedione content. Simultaneous determinations of piperazinedione were made by the "copper" method [11].

The contents of the tripeptide and "tetrapeptide" (tetra- and higher peptides) fractions were determined by differential titration in the way described previously [12]. From the amount of copper required in the titration from the "transition point" to the appearance of a suspension of $Cu(OH)_2$, the content of diglycylglycine ester was calculated as a percentage on the solid part of the reaction mixture (Curve 2, Fig. 1), and recalculation for the total amount of reaction mixture (i.e. on the weight of original ester taken) gave the amount of tripeptide ester as a percentage of the total weight of reaction mixture (Curve 2, Fig. 2). The data given show clearly that the greatest amount of diglycylglycine ester is formed after 5-6 hours from the start of the reaction. At later stages of the reaction, changes in the formation of tripeptide esters proceed much more slowly. From the fifth hour onwards the reaction mixture becomes completely solid under the conditions of the experiment, and reaction proceeds principally in a heterogeneous phase, a fact that probably determines the low rate at which the further disappearance of diglycylglycine ester from the reaction mixture occurs. Titration of the polycondensation product of glycine ethyl ester during the first hour of reaction is extremely difficult owing to the presence of considerable amounts of diglycine ester.

The data obtained on the "tetrapeptide" fraction by the same titration with 0.04 M $CuSO_4$ are shown on Curve 3, Fig. 1 (content of the solid phase). Already in the first stages of the reaction (1.5-2 hours), a certain amount of "tetrapeptide" fraction can be detected by titration with $CuSO_4$ in alkaline medium.

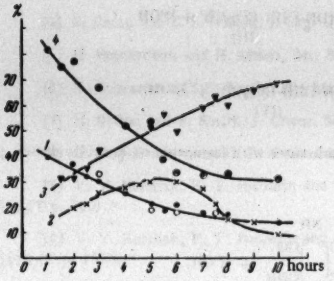


Fig. 1. Compositions of polycondensation products of glycine ethyl ester (%): 1) piperazinedione (●-determined by increase in amine nitrogen, ○-determined by the "copper" method); 2) diglycylglycine ethyl ester (×); 3) "tetrapeptide" fraction (▼); 4) free glycine ethyl ester (⊖).

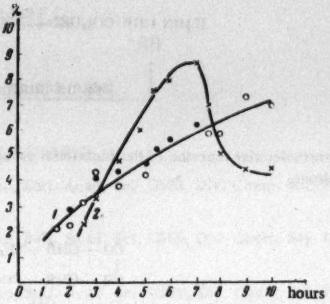


Fig. 2. Piperazinedione and diglycylglycine contents (% on original weight of monomer): 1) piperazinedione; 2) diglycylglycine ethyl ester.

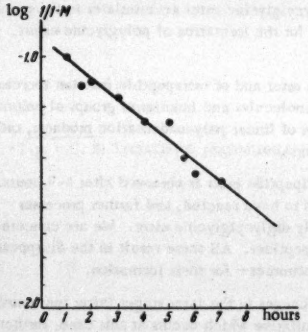


Fig. 3. Amount of glycine ethyl ester bound (M).

Unchanged monomer was washed out of the solid part with absolute ether, and was weighed after the ether had been removed under reduced pressure (10 mm, 35°). The conditions of the vacuum removal of ether were shown by experiment to be such as to ensure the complete removal not only of ether, but also of the ethanol separating during the reaction. The residual liquid was pure monomer (it gave the theoretical amount of amine nitrogen).

Quantitative data on unchanged monomer are given on Curve 4, Fig. 1, and in Fig. 3. As will be seen from Fig. 3, the experimental points fit closely to a straight line, which indicates a first-order reaction for the disappearance of monomer.

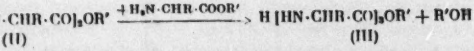
DISCUSSION OF RESULTS

As in other reactions of the same type, the primary act in the polycondensation of α-amino esters consists in reaction between two monomer molecules with formation of the dimer ester:

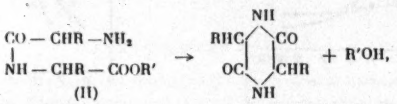
$$NH_2 \cdot CHR \cdot COOR' + NH_2 \cdot CHR \cdot COOR' \longrightarrow H[HN \cdot CHR \cdot CO]_2OR' + R'OH.$$

(I) (II)

It is possible also that all four functional groups of two monomer molecules might react simultaneously with formation of a cyclic dimer, but this reaction is of low probability, since special conditions of spatial disposition of one monomer molecule with respect to the other will be required. It is very much more probable that the dimer (II) will be formed and will undergo further transformations in two directions: a) reaction with monomer or with more dimer ester (II) with formation of linear peptides (III) and (IV):



b) intramolecular reaction of the functional groups of the dipeptide ester with formation of a cyclic dimer, piperazinedione



i.e. termination of the chain at the dimer stage.

The amount of piperazinedione resulting from the polycondensation depends on which of these two ways the process takes. Our results give a quantitative estimate of the relative extents of reactions (a) and (b), both in the initial stage of the polycondensation of glycine ethyl ester, and also in subsequent stages. The high content of piperazinedione in the first hours (1-2 hours) of the reaction is worthy of attention (it forms up to 40% of the whole solid phase; see Curve 1, Fig. 1). There is reason to suppose that at still earlier stages of the process the amount is still greater. Thus, at the start of the polycondensation reaction of glycine ethyl ester, cyclization and linear-polymer formation proceed at almost the same rate, but as diglycylglycine ester accumulates in the reaction mixture (Curve 2, Fig. 1), monomer begins to be used at a greater rate for the formation of polyglycine esters, so that the piperazinedione content of the polycondensate diminishes.

There is reason to suppose that, as the amount of diglycylglycine ester and of tetrapeptide fraction increases in the reaction mixture, the probability of reaction between monomer molecules and functional groups of polymer molecules increases. In this lies the cause of the preferential formation of linear polycondensation products, rather than cyclic products, in the succeeding stages of reaction (after five hours).

As will be seen from Curve 2, Fig. 1, the maximum content of tripeptide ester is observed after 5-7 hours. It is after just this period of time that the bulk of the monomer is found to have reacted, and further processes can occur only by reaction between esters of lower peptides, particularly diglycylglycine ester. We are concerned here with reactions with esters of monomer, dimer, trimer, and higher peptides. All these result in the disappearance of tripeptide esters, as these no longer have an adequate source – the monomer – for their formation.

The fact that the content of triglycine ester suffers less notable changes in the later stages (after ten hours) is probably to be explained by the solidification of the whole reaction mixture which occurs at this time; further reaction then has to occur in the solid phase.

SUMMARY

1. The composition of the polycondensation product of glycine ethyl ester in presence of 2% of carbon dioxide at 40° was investigated at various stages of the process. The contents of free monomer, piperazinedione, and diglycylglycine were determined quantitatively.

2. It was shown that the reaction of monomer is of first order. In the early stages of reaction (2-3 hours) there is preferential formation of piperazinedione. In later stages the relative amount of piperazinedione falls as a result of the rapid accumulation of linear-polycondensation products.

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POLYMERIZATION AND COPOLYMERIZATION OF ALKENYLSILANES UNDER HIGH PRESSURE

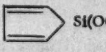
COMMUNICATION 3

A. M. Polyakova, V. V. Korshak, A. A. Sakharova, A. D. Petrov, and V. F. Mironov and G. I. Nikishin

We have previously [1] carried out the radical polymerization (in presence of tert-butyl peroxide) of nineteen alkenylsilanes of various structures at 130° under a pressure of 5500 atm. It was shown that, whereas monoalkenylsilanes form liquid polymers (from dimers to hexamers), polyalkenylsilanes (di-, tri-, and tetra-allylsilanes, and tetrakis-2-methylallylsilanes) polymerize with exclusive formation of three-dimensional polymers having a decomposition temperature of above 250°. Also, it was established that there is a difference in the tendencies of 1- and 2-alkenylsilanes to undergo polymerization, the cases examined being allyltriethylsilane and triethylvinylsilane, of which the first polymerizes as far as the pentamer, whereas the second forms an octamer.

It was noted that increase in pressure results in a higher rate of polymerization and in the formation of polymers of higher molecular weight. Thus, diallyldimethyl- and diallylmethylphenyl-silanes form three-dimensional polymers under a pressure of 5500 atm, whereas they do not polymerize at all under atmospheric pressure, other conditions being the same. At high pressure (5500 atm) triallylmethylsilane polymerizes to a glassy solid – a three-dimensional polymer – in six hours, whereas in absence of high pressure a gel-like polymer is obtained. In the polymerization of triethylvinyl- and allyltributylsilanes at atmospheric pressure the products are of lower molecular weight and are obtained in lower yield than in the polymerization of these substances at high pressure.

In the present paper (Tables 1-3) we give our results on the polymerization of forty-seven alkenylsilanes, and these enable us to give a considerably more complete characterization of the tendency of sila-olefins to polymerize. The results show that alkenyltrichlorosilanes, such as trichloro(2-methylallyl)silane and trichlorovinylsilane [2], do not polymerize to an appreciable extent; the polymerization of alkenyltrialkylsilanes goes very much better, and the degree of polymerization is particularly high in the case of alkenyltrialkoxysilanes.

We, like Kanasashi [3], are inclined to explain this behavior of the alkoxy compounds as the result of the free rotation of the OR group, a view that has already been indicated by B. A. Arbuzov and Shavsha [4]. We must point out, however, that such free rotation of alkoxy groups does not occur in all cases. In a study of the polymerization of cyclopentadienyltriethoxysilane  $Si(OC_2H_5)_3$ under the same standard conditions, we found that this compound does not polymerize, whereas cyclopentadienyltrimethylsilane $Si(CH_3)_3$, forms a polymer of molecular weight 1334 (decamer).

We must point out also the low activity of alkenylsilanes in catalytic polymerization (in presence of $AlCl_3$). Kanasashi [3] found that the polymerizaton of trimethylvinylsilane by the radical scheme results in the formation of a trimer, but polymerization by the ionic scheme (in presence of $AlCl_3$) does not occur; similarly, we found

TABLE 1

Polymerization of 1-Alkenylsilanes (Vinylsilanes)

No.	Organosilicon monomer	Pressure (atm)	Character of product	Polymerization product		
				Molecular weight (mean)	Degree of polymerization	Yield of polymer (%)
1	$(C_2H_5)_3SiCH{=}CH_2$	5500	Clear colorless viscous mass	1109	8	36.6
1a	$(C_2H_5)_3SiCH{=}CH_2$	1	Colorless oil	653	4	24,9
2	$(C_2H_5)_2SiC(CH_3){=}CH_2$	5500	Dark-yellow, viscous	588	4	19.3
3	$(C_2H_5)_2SiCH{=}CH{-}CH_3$	5500	Yellowish liquid	378	2	9.23
4	$(C_2H_5)_2SiCH{=}C(CH_3){-}CH_3$	5500	Ditto	630.4	4	9.0
5	$(CH_3)_2SiC(CH_3){=}CH_2$	5500	Dark-colored oily liquid	230	2	5.2
6	$(CH_3)_2SiCH{=}CH{-}CH_3$	5500	Does not polymerize			
7	$(CH_3)_2SiCH{=}C(CH_3){-}CH_3$	5500	Does not polymerize			
8	$(C_2H_5)_2SiCH{=}CHSi(C_2H_5)_3$	5500	Yellowish polymer	409	2	10.0
9	$(CH_3)_2SiCH{=}CHSi(CH_3)_3$	5500	Does not polymerize			
10*	$(CH_3)_2Si{<}^{(CH_3)_2Si}{>}C{=}CH_2$	5500	Yellowish liquid	918.5	5	56.0
11*	$(CH_2{=}CH)_4Si$	5500	Yellowish solid polymer	Three-dimensional polymer		
12	$(C_2H_5)_2SiCH{=}CHCl$	5500	Does not polymerize			
13	$(CH_3)_2SiCH{=}CHCl$	5500	Does not polymerize			
14	$(CH_3)_2Si{<}^{CH=CH_2}_{CH=CH_2}$	5500	Does not polymerize			
15	$\left[(CH_3)_2Si{<}^{CH=CH_2}_{CH=CH_2}\right]_2$	5500	Yellowish viscous liquid	1431	12.7	26.0

* Synthesized by V. G. Glukhovtsev.

that triethyl(2-methylpropenyl)silane forms a tetramer by radical polymerization, but a dimer by ionic polymerization. Sommer and Tyler [5] also observed the polymerization of an alkenylsilane (allyltrimethylsilane) in presence of $AlCl_3$ with formation of a product of low molecular weight.

In the synthesis of dimethyldivinylsilane, in addition to monomer we obtained also dimer. The monomer, which was found to be not altogether pure, did not polymerize (the lack of any tendency for dimethyldivinylsilane to undergo radical polymerization was indicated also by Kanasashi [3]). Under the polymerization conditions, the dimer was converted into decamer.

Tetravinylsilane, which was prepared for the first time, readily polymerized with formation of a three-dimensional polymer. One of the most interesting of our conclusions, which was based on a very large number of examples, was the high tendency of alkenyltriethylsilanes to polymerize, as compared with that of alkenyltrimethylsilanes. Thus, propenyltriethylsilane forms a dimer under conditions under which propenyltrimethylsilane does not polymerize, and similarly isopropenyltriethylsilane polymerizes to a tetramer, but isopropenyltrimethylsilane only to a dimer. This effect of ethyl groups was observed also in the case of 3-alkenylsilanes. 3-Butenyltriethylsilane polymerizes to a heptamer, whereas 3-butenyltrimethylsilane forms only a dimer under the same conditions.

TABLE 2

Polymerization of 2-Alkenylsilanes

No.	Organosilicon monomer	Pressure (atm)	Character of product	Polymerization product		
				Molecular weight (mean)	Degree of polymerization	Yield of polymer (%)
1	$(C_2H_5)_2SiCH_2—CH=CH_2$	5500	Colorless oil	781	5	20.0
2	$(CH_3)_2SiCH_2—CH=CH_2$	5500	Ditto	477	4	43.9
3	$Cl_2SiCH_2—C(CH_2)=CH_2$	5500	Very small amount of dark-colored product			
4	$(CH_3)_2ClSiCH_2—C(CH_3)=CH_2$	5500	Yellowish viscous liquid	889	6	3.7
5	$(CH_3)_2C_6H_5SiCH_2—CH=CH_2$	5500	Colorless oil	921	5	22.1
6	$(n\text{-}C_4H_9)_2SiCH_2—CH=CH_2$	5500	Ditto	734	3	43.2
6a	$(n\text{-}C_4H_9)_2SiCH_2—CH=CH_2$	1	Ditto	526	2	19.3
7	$(C_2H_5O)_2SiCH_2—CH=CH_2$	5500	Viscous mass	1266	6	16.6
8	$(C_2H_5)_2Si(CH_2—CH=CH_2)_2$	5500	Yellowish solid polymer	Three-dimensional polymer		~100
8a	$(C_2H_5)_2Si(CH_2—CH=CH_2)_2$	3500	Dark-yellow viscous mass	4112	13	25
9	$(CH_3)_2Si(CH_2—CH=CH_2)_2$	5500	Clear solid	Three-dimensional polymer		~100
9a	$(CH_3)_2Si(CH_2—CH=CH_2)_2$	3500	Benzene-soluble solid	1256	8	30.8
9б	$(CH_3)_2Si(CH_2—CH=CH_2)_2$	1	Does not polymerize			
10	$(C_2H_5)HSi(CH_2—CH=CH_2)_2$	5500	Yellowish solid	Three-dimensional polymer		~100
10a	$(C_2H_5)HSi(CH_2—CH=CH_2)_2$	1	Yellowish, viscous	433	3	13.9
11	$(CH_3)HSi(CH_2—CH=CH_2)_2$	5500	Yellowish solid	Three-dimensional polymer		~100
12	$(CH_3)(C_6H_5)Si(CH_2—CH=CH_2)_2$	5500	Yellowish solid	Three-dimensional polymer		~100
12a	$(CH_3)(C_6H_5)Si(CH_2—CH=CH_2)_2$	1	Does not polymerize			
13	$(C_6H_5)_2Si(CH_2—CH=CH_2)_2$	5500	Yellowish solid	Three-dimensional polymer		~100
14	$(CH_3)(\alpha\text{-}C_{10}H_7)Si(CH_2—CH=CH_2)_2$	5500	Dark-yellow viscous mass	466	2	18.2
15	$(C_6H_7)HSi(CH_2—CH=CH_2)_2$	5500	Yellowish solid polymer	Three-dimensional polymer		~100
16	$(CH_3)_2Si(CH_2—C(CH_3)=CH_2)_2$	5500	Benzene-soluble yellowish solid	3250	20	38
17	$(CH_3)Si(CH_2—CH=CH_2)_3$	5500	Colorless solid	Three-dimensional polymer		~100
17a	$(CH_3)Si(CH_2—CH=CH_2)_3$	1	Gel-like product			
18	$(CH_3)Si(CH_2—C(CH_3)=CH_2)_3$	5500	Colorless solid	Three-dimensional polymer		~100
19	$Si(CH_2—CH=CH_2)_4$	5500	Ditto	»		~100
20	$Si(CH_2—C(CH_3)=CH_2)_4$	5500	Ditto	»		~100

We are inclined to explain these facts by the presence of σ,σ-conjunction in compounds containing triethylsilyl radicals, whereas this is absent in compounds containing trimethylsilyl radicals:

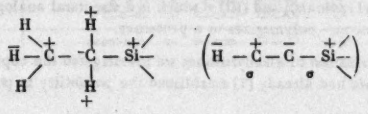


TABLE 3

Polymerization of 3-, 4-, and 5-Alkenyl- and Cyclopentadienyl-silanes

No.	Organosilicon monomer	Pressure (atm)	Character of product	Polymerization product		
				Molecular weight (mean)	Degree of polymerization	Yield of polymer (%)
1	$(C_2H_5)_3SiCH_2—CH_2—CH=CH_2$	5500	Yellowish, viscous	1157	7	20.7
2	$(CH_3)_3SiCH_2—CH_2—CH=CH_2$	5500	Yellowish oil	236	2	28.5
3	$(C_2H_5)_2CH_3SiCH_2—CH_2—CH=CH_2$	5500	Thick colorless oil	726,5	5	74.3
3a	$(C_2H_5)_2CH_3SiCH_2—CH_2—CH=CH_2$	1	Ditto	381	2	13.5
4	$(C_2H_5)(CH_3)_2SiCH_2—CH_2—CH=CH_2$	5500	Ditto	609,8	4	59.1
5	$(C_2H_5)_2SiCH(CH_3)—CH_2—CH=CH_2$		Thick oil	724,1	4	33.9
5a	$(C_2H_5)_2SiCH(CH_3)—CH_2—CH=CH_2$	1	Does not polymerize			
6	$(CH_3)_2SiCH_2—CH_2—C(CH_3)=CH_2$	5500	Thick mass	332	2	6.6
7	$(C_2H_5)_2Si(CH_3)—CH_2—CH(CH_3)—CH=CH—CH_3$	5500	Yellowish viscous liquid	830	4	3,7
8	$(C_3H_7)_2SiCH_2—CH(CH_3)—CH_2—CH=CH_2$	5500	Clear, viscous	3374	14	72.9
8a	$(C_3H_7)_2SiCH_2—CH(CH_3)—CH_2—CH=CH_2$	1	Yellowish, viscous	712	3	9.8
9	$(n\text{-}C_4H_9)_2SiCH_2—CH(CH_3)—CH_2—CH=CH_2$	5500	Clear, viscous	3970	14	48.5
9a	$(n\text{-}C_4H_9)_2SiCH_2—CH(CH_3)—CH_2—CH=CH_2$	1	Yellowish, viscous	1258	4	6.5
10	$(CH_3)_2SiCH_2—CH_2—CH_2—CH_2—CH=CH_2$	5500	Clear, viscous	979	6	70.0
11		5500	Does not polymerize			
12		5500	Light-brown viscous mass	I: 220.4 II: 1334	2 10	35 23

We have previously observed exaltation of molecular refraction in compounds containing triethylsilyl radicals, a fact that again supports the view that a conjugated system is present.

In the present investigation, as in the previous [1], we have established, on the basis of a large number of examples, that increase in pressure results in a higher rate of polymerization and the formation of polymers of higher molecular weight. The effect of pressure is particularly notable in the case of dialkenylsilanes. Whereas diallyldiethyl- and diallyldimethyl-silanes polymerize to three-dimensional polymers under a pressure of 5500 atm, the same silanes form soluble solid polymers under a pressure of 3500 atm; Finally, it should be noted that, in the present investigation, the polymerization of sila-olefins containing two silicon atoms has been carried out for the first time – the polymerization of 1,2-bistrimethylsilylethylene (I), 1,2-bistriethylsilylethylene (II), and 1,1-bistrimethylsilylethylene (III),. It was established that (I) does not polymerize, (II) forms a dimer (a further example of the effect of ethyl radicals), and (III) – which is a structural analog of 2-methylpropene, whereas (I) is a structural analog of 2-butene – polymerizes to a pentamer.

Apart from the polymerization of alkenylsilanes we investigated the copolymerization of alkenylsilanes with methyl methacrylate. We had already [7] established the possibility in principle of obtaining copolymers

TABLE 4

Copolymerization of Alkenylsilanes with Methyl Methacrylate

No.	Sila-olefin	Relative amounts in original mixture (moles)		Polymerization conditions		Character of polymer	Composition of polymer (%)		T_v	T_f	η_{sp}/c	Elementary composition of copolymer					n/m
												Found (%)			Calculated from % Si		
		MMA*	Sila-olefin	Pressure (atm)	Duration (hours)		Soluble	Insoluble				C	H	Si	C	H	
1	—	1	0	5500	6	Transparent solid	100	—	96.5	—	1.177						
2	—	1	0	1	6	Ditto	100	—	91	—	0.809						
3	$(C_6H_5)(CH_3)_2SiCH_2—CH=CH_2$	6	1	5500	6	» »	100	—	94	173	0.818	59.33	8.26	1.63	61.53	8.11	15.4
4	$(C_6H_5)(CH_3)_2SiCH_2—CH=CH_2$	6	1	1	6	» »	100	—	88	154	0.366	60.41	8.38	0.79	60.78	8.07	33.8
5	$(C_6H_5)CH_3Si(CH_2—CH=CH_2)_2$	11.7	1	5500	6	» »	17.5	82.5	b) 91	b) 191	0.712	a)**61.10	8.54	1.29	61.51	8.08	19.7
												b) 59.35	7.88	1.25	61.59	8.08	20.4
6	$(C_6H_5)CH_3Si(CH_2—CH=CH_2)_2$	11.7	1	1	6	» »	22.5	77.5	b) 80.5	b) 156	0.510	a) 61.51	8.37	1.30	61.61	8.08	19.6
												b) 58167	7.61	1.92	62.42	8.13	14,4
7	$(C_6H_5)CH_3Si(CH_2—CH=CH_2)_2$	39	1	5500	6	» »	100	—	66	152.5	0.641	59.31	8.37	0.33	60.41	8.02	82.4
8	$(C_6H_5)CH_3Si(CH_2—CH=CH_2)_2$	39	1	1	6	» »	100	—	72.5	146	0.474	60.0	8.39	0.87	61.08	8.06	30.2
9	$(CH_3)_2Si(CH_2—CH=CH_2)_2$	14.5	1	1	6	» »	49.1	50.9	—	—	0.605	a) 60.40	8.38	0.55	60.23	8.10	49.6
												b) 57.77	7.76	1.71	60.73	8.29	15.0
10	$(CH_3)_2Si(CH_2—CH=CH_2)_2$	14,5	1	1	50	» »	—	100	—	—	—	59.83	8.33	0.63	60.28	8.11	43.14
11	$(CH_3)_2Si(CH_2—CH=CH_2)_2$	1	1	1	50	» »	—	100	64.2	145	—	59.77	8.90	8.40	63.58	9.43	1.94
12	$(CH_3)_2Si(CH_2—C(CH_3)=CH_2)_2$	7.2	1	5500	6	» »	91.6	8.4	a) 91	a) 178.5	0.783	a) 60.73	8.38	0.60	60.40	8.14	45.09
												b) 60.11	8.43	1.43	60.86	8.32	17.9
13	$(CH_3)_2Si(CH_2—C(CH_3)=CH_2)_2$	9.9	1	1	6	» »	100	—	121	173	0.372	60.11	8.19	0.62	60.43	8.14	43.6
14	$(CH_3)_2Si(CH_2—C(CH_3)=CH_2)_2$	1	1	1	50	Mixture of liquid and solid***	100	—	97	155	0.424	61.58	8.53	0.73	60.40	8.14	36.7

* MMA = methyl methacrylate.

** a) Results of elementary analysis and the values of T_v and T_f for the soluble part of the polymer. b) The same for the insoluble part.

*** The table gives the results of elementary analysis and the value of η_{sp}/c for the solid product.

of alkenylsilanes without the use of high pressures, polyalkenylsilanes being used as organosilicon components. It was found that, of the polyalkenylsilanes investigated, only tetrakis-2-methylallylsilane formed a three-dimensional copolymer with methyl methacrylate. The others – dimethylbis-2-methylallyl- and diallylmethylsilanes – formed linear copolymers. Allyltributylsilane proved to be incapable of copolymerization with methyl methacrylate. In the present paper we give data (Table 4) on the copolymerization of mono- and di-alkenylsilanes with methyl methacrylate, which was carried out both at high pressure (5500 atm) and at atmospheric pressure. Allyldimethylphenyl-, diallyldimethyl-, diallylmethylphenyl-, and dimethylbis-2-methylallyl-silanes were investigated.

In these experiments the relative amounts of sila-olefin and methyl methacrylate and the duration of reaction were varied. We confirmed the previously established fact [7] of the formation of soluble copolymers of dimethylbis-2-methylallylsilane with methyl methacrylate under atmospheric pressure. We showed also that the copolymer obtained at high pressure (5500 atm) contains a certain amount (about 8%) of insoluble, three-dimensional polymer. The other dialkenylsilanes that we studied formed mixtures of soluble and insoluble copolymers, with a considerable predominance of the latter. Also, the amount of insoluble copolymer increased both with increase in the relative amount of sila-olefin in the original mixture, and with increase in the duration of the copolymerization reaction. The formation of a greater amount of insoluble copolymer was favored also by increase in pressure. We prepared copolymers of allyldimethylphenylsilane with methyl methacrylate having silicon contents of 0.79 and 1.63%, and the viscosities (η_{sp}/c, c = g/100 ml) of these copolymers were less than those of methyl methacrylate homopolymers prepared under the same conditions. According to our experimental results, the use of high pressures during copolymerization generally results in the formation of polymers of higher viscosity than those formed at atmospheric pressure. Investigation of thermo-mechanical compression curves, which were determined for most of the polymers and copolymers obtained, showed that homopolymers of dialkenylsilanes, such as diallyldimethyl- and diallylmethylphenylsilanes, are three-dimensional: they do not soften up to temperatures of the order of 400° (at these temperatures only charring of the outer layers of the sample was observed). Copolymers of the same dialkenylsilanes with methyl methacrylate exhibit both a temperature of transition from the vitreous to the high elastic state (T_v), and also a temperature of transition to the state of viscous flow (T_f). T_v abd T_f were determined by a continuous method at a constant applied load of 0.5 kg, the diameter of the plunger being 4 mm. T_v was taken to be the temperature at which the plunger gave an impression in the sample of 0.05 mm.

A more detailed study of the physico-mechanical properties of alkenylsilane polymers and copolymers is to be the subject of further investigation.

EXPERIMENTAL

The investigation of polymerization and copolymerization under pressure was carried out under the same conditions as those described previously [1], i.e. in presence of 3% by weight of tert-butyl peroxide at 130° and 5500 atm (in some experiments a lower pressure was used). Experiments in which a high pressure was not applied were carried out in sealed glass tubes. The duration of each polymerization experiment was six hours, and in the copolymerization experiments times of 6 and 50 hours were used.

The treatment of the polymerization products of low molecular weight was carried out as described previously [1]. Macromolecular polymers (copolymers) were purified by reprecipitation from acetone with methanol. Molecular weights of low-molecular-weight polymers were determined cryoscopically in benzene. The relative viscosities of solutions of copolymers in dichloroethane were measured with an Ostwald viscometer at 20°, concentrations of 0.4 g per 100 ml being used. The compositions of the copolymers were determined from the silicon content and were calculated, as before [7], by the formula

$$\frac{n}{m} = \frac{\frac{2806}{\%\,Si} - M_2}{M_1},$$

in which n is the number of monomer residues (M_1) of methyl methacrylate and m is the number of sila-olefin residues (M_2). The results are presented in Tables 1-4.

The authors express their thanks to B. L. Tsetlin for help in the determination of the thermo-mechanical properties of polymers and copolymers and for discussion of the results.

SUMMARY

1. An investigation was made into the tendency of mono- and poly-alkenylsilanes to polymerize at ordinary and high pressures.

2. It was shown that the tendency of alkenylsilanes to polymerize varies with their structures.

3. It was shown that increase in pressure results in increase in the rate of polymerization of alkenylsilanes and in increase in the molecular weight of the resulting polymers.

4. An investigation was made into the copolymerization of methyl methacrylate with the following mono- and di-alkenylsilanes: allyldimethylphenyl-, diallyldimethyl-, diallylmethylphenyl-, and dimethylbis-2-methylallyl-silanes. Thermo-mechanical properties of the copolymers were determined.

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ALKYLATION AND DEALKYLATION OF BENZENE AND ITS HOMOLOGS IN PRESENCE OF ALUMINOSILICATES

Yu. G. Mamedaliev and G. M. Mamedaliev

The transfer of methyl groups from one aromatic hydrocarbon molecule to another and the dealkylation of alkyl-substituted aromatic compounds in the liquid phase in presence of aluminum chloride formed the subject of investigations by various workers at the end of the last century [1,2]. The practical significance of these investigations was realized during the 1914-18 war, when attention was turned to the possibility of preparing toluene from xylene and from suitable fractions of coal-tar distillate [3,4]. We studied these reactions in detail in a previous investigation [5], which was devoted to the synthesis of toluene by the alkylation and dealkylation of aromatic hydrocarbons. In this work we noted the exceptionally favorable effect of high pressure (20-25 atm) on the yield of toluene in the combined alkylation-dealkylation treatment of a mixture of xylenes, polymethylbenzenes, and benzene.

During World War II large-scale manufacture of ethylbenzene, cumene, and butylbenzenes was rapidly put into operation and later considerably extended. Industrial application was made also of the catalytic synthesis of toluene by the condensation of benzene with methanol, which was carried out over a zinc phosphate catalyst at high pressure. In the manufacture of alkylated aromatic hydrocarbons, irrespective of the kind of catalysts used and the conditions of the reaction, some di-, tri-, and poly-alkylbenzenes boiling above the upper limit for aviation gasoline were always formed [6,7]. In fact, with the coming of the above-discussed manufacture of toluene and alkylated aromatics, quantities of polyalkylbenzenes were made available, and these, together with the corresponding fraction from coal and pyrolysis tar, formed an adequate base of raw materials for industrial dealkylation.

In the last decade, in conjunction with the extensive application of aluminosilicate catalysts in the treatment of petroleum, successful application was made of these same catalysts for the dealkylation of polyalkylbenzenes. More important results were obtained when aluminosilicates were used in the combined alkylation-dealkylation of mixtures of benzene and aromatic hydrocarbons of differing degrees of substitution.

One of the authors of the present paper [8] has investigated the reactions of dealkylation and intermolecular alkyl transfer for diisopropylbenzene in presence of natural aluminosilicate catalysts. Experiments were carried out over the temperature range 350-450° and pressure range 20-60 atm for various reaction times, and the relative extents to which the main and subsidiary reactions occurred were determined.

Moldavsky and Bezdel [9] studied the mechanism of the dealkylation of various alkylbenzenes over the activated natural aluminosilicate humorin. They showed that, under their conditions (temperature 410°, rate 1.5 : 1), the readiness with which an alkyl group is eliminated increases with increase in the degree of polarization of the bond between the alkyl and phenyl groups of the original alkylbenzene. A paper by Hansford, Myers, and Sachanem [10] presents the results of experiments with xylene, 1,2,4-trimethylbenzene, methylnaphthalene, and diethylbenzene in presence of aluminosilicates at atmospheric pressure in the temperature range 450-540°.

In the catalytic treatment of tar obtained by the pyrolysis of petroleum, a substantial increase in the yield of toluene is obtained in presence of a synthetic aluminosilicate catalyst; to a considerable extent this is the result of combined alkylation-dealkylation reactions of aromatic hydrocarbons and of the hydrostabilization of olefins [11]. A study of the nature of the unsaturated hydrocarbons present in pyrolysis tar and thermal-cracking kerosene [12] showed that they are mainly cyclic compounds, which, in presence of aluminosilicate,

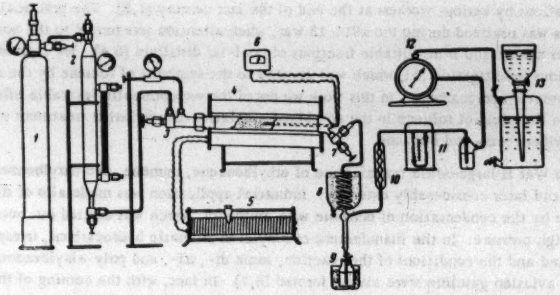
are converted into aromatic hydrocarbons as a result of a hydrogen-transfer reaction.

Investigations worthy of attention are those of Johanson and Watson [13] on the combined alkylation-dealkylation of a mixture of benzene and xylene in presence of aluminosilicates at high pressure. Among recent investigations the work of Roberts and Good [14] is of interest; these workers compared the readiness with which cumene and some of its derivatives are dealkylated in presence of aluminozirconosilicates at 400-500° at atmospheric pressure. The dealkylation reaction was carried out also in presence of alumina activated with hydrofluoric acid [15].

In the further development of our earlier investigations on combined alkylation-dealkylation of aromatic hydrocarbons in presence of heterogeneous catalysts, which were carried out in 1940-45, we undertook the present investigation. Part of this investigation, which is concerned with combined methylation-demethylation, is described below.

EXPERIMENTAL

The experiments were carried out in a laboratory continuous-flow apparatus, which is shown diagrammatically below.



Continuous-flow reactor for the catalytic treatment of hydrocarbons under pressure: 1) nitrogen cylinder; 2) vessel for raw material; 3) reactor; 4) tube furnace; 5) rheostat; 6) galvanometer; 7) reduction valve; 8) condenser; 9) receiver; 10) gas condenser; 11) flow-meter; 12) flow indicator; 13) gas meter.

The liquid reaction products were fractionated through a 20-25 plate laboratory column. Group chemical compositions were determined for the raw material and the catalyzates. Gases were analyzed in an Orsat apparatus. Gases obtained in experiments carried out under optimum conditions were analyzed in Podbielniak and TsIATIM (Central Research Institute for Aviation Fuels and Oils) apparatuses. For the toluene obtained, determinations were made of density, iodine and bromine values, acidity, refractive index, sulfonatability, etc. In order to obtain data for determining the material balance and the basic parameters of the process (temperature, pressure, rate of passage, duration of the reaction cycle), series of experiments were carried out with various mixtures. Synthetic aluminosilicates were used as catalysts.

Catalytic Dealkylation of o- and m-Xylenes in presence of Benzene

Experiments on the dealkylation of m- and o-xylenes with simultaneous alkylation of benzene were made over synthetic aluminosilicates under known optimumconditions: 15 atm, 525°, passage of 0.5 volume raw material per one volume of catalyst per hour, duration of cycle 50 minutes. The raw materials were cryoscopic benzene (boiling range 79.74-80.13°, bromine value 0.03, density 0.8782, sulfonatability 99.6%) and chemically pure o-xylene (boiling range 143.2-144°, density 0.8799, refractive index 1.5050, sulfonatability 100%), which analysis by the oxidation method showed content of 98.7% of o-xylene and 1.3% of m-xylene.

The experiments were carried out for a molar ratio of benzene to o-xylene of 2 : 1. According to rectification data, the benzene content of the mixture was 58% by weight, and the o-xylene content 35% by weight. It was found that at 5 atm and 525° a single passage of the mixture over the catalyst resulted in the formation of 97.1 % of catalyzate, 0.7% of gas, and 0.8% of coke. The catalyzate contained 20.1% of toluene. The benzene content fell from 58% in the raw material to 49.4% in the catalyzate. A considerable part of the o-xylene was demethylated to toluene, and as a result the xylene content fell from 35% to 11-12%. It is interesting to note that o-xylene is isomerized over synthetic aluminosilicate into the meta and para isomers with a resulting displacement in the boiling range of the fraction and a corresponding lowering of the density and refractive index. A little trimethylbenzene is formed.

Increase in pressure to 15 atm resulted in an increased yield of toluene. Its content in the catalyzate was 27-28% by weight. The process was characterized by the formation of comparatively large amounts of coke (1.9-2.2%) and gas (1.7-2.3%). The yield of catalyzate was 94.5-95.2% by weight on the raw material.

The formation of 27-28 g of toluene and about 3-3.5 g of a trimethylbenzene fraction resulted from the alkylation of 9-10 g of benzene and the dealkylation of 17.7-19.2 g of o-xylene. Hence, the formation of toluene proceeds to the extent of about 35-40% on account of the alkylation of benzene and to the extent of 60-65% on account of the dealkylation of xylene. Increase in pressure causes the process to proceed somewhat further: the various reactions are affected to about the same extent by increase in pressure, and the relative extents to which these reactions contribute to the formation of toluene remain at about the same values as at a pressure of 5 atm.

Over aluminosilicates, dealkylation of o-xylene with simultaneous alkylation of benzene proceeds extremely smoothly without any accompanying decomposition and condensation reactions. The formation of unsaturated hydrocarbons and products of higher molecular weight is not observed. The catalyzates have zero iodine value and a sulfonatability of 100%. In all of its standardized characteristics, the toluene isolated from the catalyzate is completely up to standard: its bromine value does not exceed 0.03, its density varies over the range 0.8665-0.8670, its refractive index is 1.4969-1.4972, and its sulfonatability is 100%.

Similar experiments were carried out with m-xylene. The experimental conditions and the relative amounts of the components of the mixture were the same as in the investigation of the mixture of o-xylene and benzene. The m-xylene used boiled over the range 137-139°, its density was 0.8634, its refractive index was 1.4975, and its sulfonatability was 100%. Analysis of the m-xylene by side-chain oxidation with formation of benzenedicarboxylic acids showed that the original xylene contained a little of the para isomer.

It was shown that at 5 atm the yield of catalyzate was 96.9%, and 0.09% of gas and 0.9% of coke were obtained. The toluene content of the catalyzate was 17.4%. The results obtained with m-xylene were very close to those obtained for o-xylene. Increase of the pressure to 15 atm resulted in maximum toluene formation, and the toluene content of the catalyzate then attained 28-31%.

The process was characterized by the occurrence of two main reactions: dealkylation of xylene with transfer of the methyl group to the benzene molecule, and interrelated alkylation and dealkylation of the xylene molecule. Under optimum conditions the yield of catalyzate was 94-95%, and 1.7-2.3% of gas and 1.9-2.2% of coke were obtained. The boiling limit of the catalyzate was 164°. Unsaturated hydrocarbons were absent, and the sulfonatability was 100%. The gas formed in the process consisted of methane and hydrogen.

Dealkylation of Polymethylbenzenes with Simultaneous Alkylation of Benzene

We investigated also dealkylation coupled with alkylation in a mixture of polymethylbenzenes and benzene. We studied the effect of temperature and pressure, and we established the optimum values of the parameters for toluene formation. Both a wide polymethylbenzene fraction and also its individual narrow fractions were used in the experiments. In the wide polymethylbenzene fraction there was 2.3% of toluene, 48.8% of a xylene fraction, and about 10-12% of a trimethylbenzene fraction. The amount of higher-boiling polymethylbenzenes varied over the range 20-25%. The sulfonatability of the original material was 100%, and its iodine value was zero.

The results of experiments on the catalytic treatment of a mixture of benzene and the wide polymethylbenzene fraction at a pressure of 15 atm, velocity of 0.5 : 1, duration of cycle of one hour, and weight ratio

of benzene to polymethylbenzene of 2 : 1 showed that at 450° a single passage of the mixture over the catalyst results in the formation of 96.7% of catalyzate, 1.8% of coke, and 0.2% of gas.

Toluene, which is obtained in 7.8% yield, is formed mainly on account of the conversion of polymethylbenzenes, but partly also by simultaneous alkylation of benzene. Rise in temperature to 500° results in increase in the yield of toluene, which is formed by the dealkylation and interrelated alkylation of the original aromatic hydrocarbons. At 525° the yield of toluene was 21.6%. The contents of the benzene and xylene fractions in the catalyzate were 58% and 9.6%, respectively. The yields were 94.8% of catalyzate, 2.4% of coke, and 1.8% of gas. Raising the temperature to 550°, although increasing the toluene content to 23.8%, gives comparatively high yields of coke (3.6%) and gas (3.2%) and a correspondingly lower yield of catalyzate (92.4%), so that, on the whole, the characteristics of the process are worsened. On the basis of this investigation it was established that the optimum temperature for the reaction under consideration lies in the range 500-525°.

The next series of experiments were carried out with the aim of determining the effect of pressure on the characteristics of the process. The experiments were carried out at the optimum temperature of 525°, at a velocity of 0.5 : 1, and at a cycle time of one hour. These experiments showed that some dealkylation of xylenes occurred at atmospheric pressure. The toluene content was increased from 1.8% in the raw material to 5.5% in the catalyzate. Benzene did not take part in the reaction, and the amount present remained almost unchanged. The contents of xylene and higher-boiling polymethylbenzenes fell somewhat. The residue in rectification fell from 6.1% in the raw material to 2.3% in the catalyzate. The boiling limit fell from 200° to 173°.

Increase in pressure up to 5 atm increases the rate of the reaction of demethylation of polymethylbenzenes with simultaneous methylation of benzene. The contents of benzene, xylene, and polymethylbenzene fractions are appreciably reduced. The amount of toluene in the catalyzate is 15.7%, and unsaturated hydrocarbons are absent. The maximum effect is attained at pressures of 10 and 15 atm. The toluene content of the catalyzate increases to 20.5-21.6%. Almost complete conversion of the polymethylbenzenes occurs. The benzene and xylene contents are reduced from 63.8% and 15.8%, respectively, in the raw material to 58-59% and 9-10% in the catalyzate. The boiling limit of the catalyzate is 159-162°. The toluene obtained is fully in accord with the standard specification. The use of still higher pressures (20-25 atm) has no effect on the quality of the catalyzate, but the yields of coke and gas are somewhat increased.

Investigations were carried out also on the conversion of individual fractions of the polymethylbenzenes in presence of benzene. It was shown that catalytic treatment of a mixture of a xylene fraction of b.p. 125-150° with benzene in the weight ratio of 1 : 2 at 525° and 1 atm results in insignificant formation of toluene. The toluene content was increased from 0.3% in the raw material to 3.9% in the catalyzate. There was some rise in the upper boiling limit of the catalyzate, due, no doubt, to the formation of a small amount of trimethylbenzenes by dismutation of xylene. The yields of catalyzate, coke, and gas were 97.6, 0.88, and 0.36%, respectively. Increase in pressure to 10 atm resulted in an increase of the toluene content of the catalyzate to 24.6%. The contents of benzene and xylene fractions were reduced from 57.0% and 35.8%, respectively, in the raw material to 50% and 19% in the catalyzate. The yield of catalyzate (% by weight on the raw material) was 95%, and the yields of coke and gas were 1.8% and 2.1%, respectively. The gas consisted mainly of methane (90-93% by volume) and hydrogen (7-10% by volume). The maximum effect was attained at 15 and 20 atm. The toluene content of the catalyzate was then 26.3-27%. In other respects the results were essentially the same as in the experiments carried out at 10 atm.

In all experiments, irrespective of pressure, the formation of a little methylated benzene of high boiling point was observed, and the presence of this resulted in the raising of the upper boiling limit from 142° to 164° and in an increase in the yield of the rectification residue from 1.1% to 2.2%.

The following series of experiments was carried out with a high-boiling polymethylbenzene fraction. Fractionation data indicated that this fraction contained 30.5% of trimethylbenzenes (160-172° fraction), 11.5% of tetramethylbenzenes (190-205° fraction), and 45% of penta- and hexa-methylbenzenes, boiling above 205°. From the results of experiments carried out with the high-boiling polymethylbenzene fraction it follows that a considerable part of this is converted into xylenes and toluene at atmospheric pressure. The boiling limit is lowered to 185°. The toluene and xylene contents of the catalyzate are 9% and 6%, respectively. At 5 atm the yield of toluene increases to 14.3%, and that of the xylene fraction to 8.1%. As a result of the transformations of the high-boiling fractions, the amount of residue is reduced from 13% in the

raw material to 3% in the catalyzate.

The catalyzates obtained in the experiments at 10 and 15 atm did not differ appreciably in quality. The toluene content was 17-18%. The yields of catalyzate, coke, and gas varied within the ranges 92.4 to 83%, 3.5-3.6%, and 2.0-2.1%, respectively. Increase in pressure to 20 atm resulted in a rise in the content of toluene to 21% and in the content of xylenes to 6.6%. The yields of catalyzate, coke, and gas were 91%, 4.2%, and 2.8%, respectively. Further increase in pressure to 30-40 atm had practically no effect on the quality of the catalyzate, but caused some increase in the yields of gas and coke. Hence, under the selected conditions of temperature and rate of passage of raw material, the optimum pressure is 15-20 atm.

SUMMARY

1. The catalytic treatment of a mixture of benzene, xylenes, and other polymethylbenzenes in presence of synthetic aluminosilicates is accompanied by dealkylation reactions and alkyl-transfer reactions leading to the formation of toluene in appreciable amount. The extent to which each of these reactions participitates in the process is found to be directly related to the value of the applied pressure.

2. The use of an elevated pressure is of decisive importance for maximum formation of toluene. With increase in pressure the yield of toluene increases, attaining a maximum in the range 10-20 atm. The optimum conditions for the reaction were determined.

3. The predominant reaction resulting in the formation of toluene at elevated pressure is demethylation of xylenes and polymethylbenzenes with simultaneous methylation of benzene. A small part is played in the formation of toluene by the migration of methyl groups of xylenes with formation also of trimethylbenzenes. The readiness with which methyl groups are eliminated tends to increase as their number in the benzene nucleus increases.

4. In the reaction of coupled alkylation and dealkylation in a mixture of benzene and o-xylene, isomeric transformation of o-xylene into the meta and para isomers occurs.

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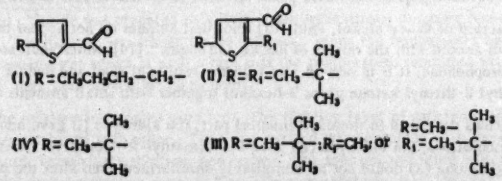
SYNTHESIS OF ALIPHATIC ALCOHOLS FROM THIOPHENE AND ITS HOMOLOGS*

Ya. L. Goldfarb and P. A. Konstantinov

As shown previously [1-7], the action of Raney nickel on thiophene derivatives can be used as a method for the preparation of aliphatic compounds. This method may be particularly useful when other methods for the synthesis of such compounds are not readily accessible. In the present investigation this is demonstrated for the case of the preparation of higher alcohols, including branched-chain alcohols having one or two quaternary carbon atoms.

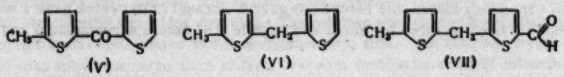
For the preparation of the original thiophene compounds having sufficiently long carbon chains we used two methods: 1) the synthesis of alkylthiophenes having the necessary number of carbon atoms and the subsequent introduction of a functional group, and 2) the synthesis of 2,2'-methylenedithiophene derivatives and their formylation.

By formylation [8] 2-butylthiophene was converted into the previously unknown 5-butyl-2-thiophenecarboxaldehyde (I). In the same way we synthesized 2,5-di-tert-butyl-3-thiophenecarboxaldehyde (II), 5-tert-butyl-2-methyl- or 2-tert-butyl-5-methyl-3-thiophenecarboxaldehyde (III), and 5-tert-butyl-2-thiophenecarboxaldehyde (IV) from the corresponding substituted thiophenes.



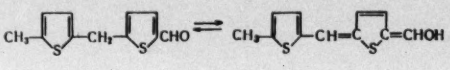
It must be pointed out that the 3-carboxaldehydes are obtained in lower yields than the 2-carboxaldehydes. For example, the yield of the aldehyde (I) was 80%, whereas the yield of the aldehyde (II) was not more than 36% on the amount of 2,5-di-tert-butylthiophene that reacted. It is noteworthy that an attempt to formylate 3,5-di-tert-butyl-2-methylthiophene was not successful, probably owing to the screening of the 4-position by two very bulky tert-butyl groups.

As starting material for the preparation of decyl and undecyl alcohols we used 5-methyl-2-thienyl 2-thienyl ketone (V), which was synthesized by the acylation of thiophene with 5-methyl-2-thiophenecarbonyl chloride. When subjected to Kizhner reduction, the ketone (V) gave 5-methyl-2,2'-methylenedithiophene (VI). This fact conflicts with the conclusions of Löfgren and Tegner [9], who asserted that di-2-thienyl ketone cannot be reduced by the Kizhner method.



* Author's Certificate No. 100, 411 (April 19, 1955).

By the formylation of (VI) we obtained 5-(5-methyl-2-thenyl)-2-thiophenecarboxaldehyde (VII). It is notable that the molecular refraction found for the aldehyde (VII) is considerably greater than the calculated value. This may be due to the occurrence of the tautomeric equilibrium:



In this connection we must refer to a recently published paper [10] which rejects the widely held view that aldehydes form only traces of the enol form.

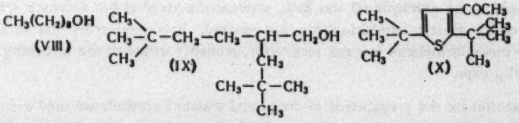
The Raney nickel required for the reaction was prepared by the method of Adkins and Billica [11]. In the treatment of the original carbonyl compound with this product, not only desulfurization occurred, but also hydrogenation of double bonds and reduction of the aldehyde or, in some cases, keto group. In this connection it must be pointed out that the available data on the behavior of ketones and keto acids in presence of Raney nickel under conditions similar to those described in the experimental part indicate that the reactions occurring are somewhat complex.

In some cases the secondary alcohol that is formed, at first may be subjected to further action by the catalyst and undergo dehydrogenation, which, as Paul showed [12], may occur at a comparatively low temperature. Hence, the fact that a compound having a C=O function may be formed during a hydrogenolysis treatment cannot always be ascribed to the preservation of the compound first formed. Available data enable us to come to the general conclusion that the nature of the product formed by the action of Raney nickel depends not only on the character of the original compound, but also on the type of solvent, the method of preparing the catalyst, the amount of catalyst, and the duration of its action.

Papa and coworkers [13] consider that, in those cases in which the C=O group is conjugated with the system of double bonds of the aromatic nucleus, reduction gives the corresponding hydrocarbons; otherwise, the process comes to an end at the secondary alcohol stage. Later, the same investigator showed [6] that, depending on the reaction conditions, 3-(2-thenoyl)propionic acid gives either 5-oxooctanoic acid or the corresponding lactone.

In work on the action of Raney nickel, Paul [12] finds that ketones do not appear to react in presence of this catalyst. This is in accord with the results of Blicke and Sheets [14], which indicate that phenyl 2-thienyl ketone gives only valerophenone; it is in accord also with the results of Hurd and Rudner [15], which show that the hydrogenolysis of methyl 2-thienyl ketone gives 2-hexanol together with small amounts of ethanol and acetaldehyde.

Under the conditions described in the experimental part, the aldehyde (I) gave nonyl alcohol (VIII) in 65% yield. Under similar conditions, the aldehyde (II) gave 5,5-dimethyl-2-neopentyl-1-hexanol (IX), but 2,5-di-tert-butyl-3-thienyl methyl ketone (X) could not be completely desulfurized even after the prolonged action of Raney nickel.•



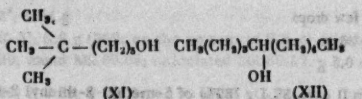
The aldehyde (IV) gave 6,6-dimethyl-1-heptanol (XI). The analysis and molecular refraction of this alcohol corresponded to the calculated values, but we did not succeed in preparing a phenyl- or naphthyl-urethan from it in a crystalline state.••

When heated with Raney nickel, the ketone (V) gave 5-decanol (XII), which gave a naphthylurethan melting at 58°. This alcohol has been prepared by Woods and Lederle [16] from 2,4-pentadienal and pentadienylmagnesium

• Boiling under reflux for 17 hours.

•• This aldehyde was synthesized by the formylation of 2-tert-butylthiophene, which we prepared by the method of Goldfarb and Korsakova [17], and also by Caesar's method [18]. The semicarbazone of this aldehyde melted at 215-216°, which agrees with Messina's result, but not with results of Sy and Buu-Hoi [7], who give m.p. 246°.

chloride with subsequent Ponndorf reduction.

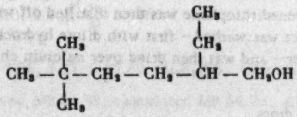


(XI) (XII)

According to these authors the naphthylurethan derived from 5-decanol melts at 56°.

As would be expected, the compound formed by the hydrogenolysis of the aldehyde (VII) was found to be undecyl alcohol, this being confirmed by comparing the melting point of its phenylurethan with that of the similar compound obtained from an authentic sample of undecyl alcohol.

Hydrogenolysis of the aldehyde (III) gave an alcohol of composition $C_{10}H_{22}O$, which was probably 2-ethyl-5,5-dimethyl-1-hexanol:



However, as the structure of the original aldehyde (III) cannot be considered to be completely established, the question of the structure of this alcohol must be regarded as an open one.

EXPERIMENTAL

5-Butyl-2-thiophenecarboxaldehyde. A mixture of 44.6 g (0.33 mole) of N-methylformanilide and 50.5 g (0.33 mole) of phosphoryl chloride was prepared in a flask fitted with stirrer, dropping funnel, calcium chloride tube, and thermometer. The mixture was stirred for 30 minutes. When the temperature had fallen to 25°, 42 g (0.3 mole) of 2-butylthiophene was added at such a rate that the temperature remained within the range 25-35°. The contents of the flask were then stirred for three hours.

On the next day the mixture was poured onto ice. The floating layer of dark-colored oil was separated, and the aqueous layer was extracted with ether. The ether extract was combined with the organic layer and washed with 10% hydrochloric acid, bicarbonate solution, and water. The solution was dried with magnesium sulfate, solvent was driven off, and distillation then gave 42.7 g of impure aldehyde, b.p. 138-146° (22 mm) and n_D^{20} 1.5493, and about 2 g of resinous residue.

Refractionation gave 40.6 g (80%) of product, b.p. 143-146° (22 mm); n_D^{20} 1.5490; d_4^{20} 1.0557; found MR 50.34; calculated MR 50.68.

Found %: C 64.47, 64.58; H 7.25, 7.35; S 18.57, 18.79. $C_9H_{12}OS$. Calculated %: C 64.24; H 7.20; S 19.05.

After being recrystallized from aqueous alcohol, the oxime of 5-butyl-2-thiophenecarboxaldehyde melted at 61-62°.

Found %: C 58.79, 58.81; H 7.06, 7.02. S 17.75, 17.42. $C_9H_{13}NOS$. Calculated %: C 59.01; H 7.10; S 17.54.

5-Methyl-2-thienyl 2-Thienyl Ketone. A mixture of 36.4 g (0.218 mole) of 5-methyl-2-thiophenecarbonyl chloride, 18.3 g of thiophene, and 20 ml of dry benzene was prepared in a flask fitted with mercury-sealed stirrer, thermometer, calcium chloride tube, and dropping funnel. The solution was cooled to 0°, and 21.4 ml (0.18 mole) of freshly distilled stannic chloride was added dropwise. The mixture was stirred for a further period of one hour at room temperature, and it was then treated with 10% hydrochloric acid. The benzene layer was separated, washed with water, and dried with anhydrous magnesium sulfate. Vacuum distillation (6 mm) of the reaction product gave

Fraction I, b.p. to 185°; a few drops
Fraction II, b.p. 185-186; 38 g
Residue 0.5 g

Refractionation of Fraction II gave 37.1 g (82%) of 5-methyl-2-thienyl 2-thienyl ketone, m.p. 46-48°, raised by recrystallization from 70% alcohol to 48.5-50°.

Found %: C 57.53, 57.53; H 3.86, 3.97; S 30.71, 30.90. $C_9H_8OS_2$. Calculated %: C 57.70; H 3.84; S 30.77.

After recrystallization from aqueous alcohol, the oxime of this ketone melted at 98-99°.

Found %: N 6.12, 6.22. $C_9H_9NOS_2$. Calculated %: N 6.27.

5-Methyl-2,2'-methylenedithiophene. A mixture of 12.2 g (0.06 mole) of 5-methyl-2-thienyl 2-thienyl ketone, 12 ml of 85% hydrazine hydrate, and 70 ml of diethylene glycol was heated to 50-60°, and 12 g (0.2 mole) of potassium hydroxide was added. The mixture was heated until gas ceased to be evolved (about four hours). The 5-methyl-2,2'-methylenedithiophene was then distilled off with superheated steam. The distillate was extracted with ether, the extract was washed – first with dilute hydrochloric acid, then with sodium bicarbonate solution, and finally with water – and was then dried over calcium chloride. Vacuum distillation (6 mm) of the reaction product gave

Fraction I, b.p. to 115°; a few drops
Fraction II, b.p. 116-117°; 7.9 g (61%)
Residue 2.1 g of resin

Refractionation of Fraction II gave 6.7 g of 5-methyl-2,2'-methylenethiophene, b.p. 116-117° (6 mm); n_D^{20} 1.5946; d_4^{20} 1.1616; found MR 56.77; calculated MR 56.11.

Found %: C 61.85; H 5.25; S 32.97. $C_9H_{10}S_2$. Calculated %: C 61.90; H 5.15; S 32.97.

5-(5-Methyl-2-thenyl)-2-thiophenecarboxaldehyde. Reaction between 6.4 g (0.033 mole) of 5-methyl-2,2'-methylenedithiophene, 8.4 g (0.062 mole) of N-methylformanilide, and 9.4 g (0.062 mole) of phosphoryl chloride gave 2.7 g of unchanged 5-methyl-2,2'-methylenedithiophene and 3.3 g (44%) of 5-(5-methyl-2-thenyl)-2-thiophenecarboxaldehyde. b.p. 156-158° (3 mm); n_D^{20} 1.6218; d_4^{20} 1.2256; found MR 63.76; calculated MR 60.74.

Found %: C 59.32, 59.58; H 4.54, 4.65; S 28.71, 28.56. $C_{11}H_{10}OS_2$. Calculated %: C 59.42; H 4.53; S 28.84.

After two recrystallizations from 80% alcohol, the oxime of the aldehyde melted 119.5-121°.

Found %: N 5.7. $C_{11}H_{11}NOS_2$. Calculated %: N 5.9.

5-tert-Butyl-2-thiophenecarboxaldehyde. Reaction between 21 g (0.15 mole) of 2-tert-butylthiophene, 20.2 g (0.15 mole) of N-methylformanilide, and 23 g (0.15 mole) of phosphoryl chloride gave 24.5 g of a product, which was fractionated at 25 mm:

Fraction I, b.p. to 135°; a few drops
Fraction II, b.p. 135-136°; 23.6 g (91%); n_D^{26} 1.5441.
Residue in flask 0.9 g

After being recrystallized twice from ethanol, the semicarbazone of the aldehyde melted at 215-216°.

2,5-Di-tert-butyl-3-thiophenecarboxaldehyde. Formylation was carried out at 55-60°, the reactants being 49 g (0.25 mole) of 2,5-di-tert-butylthiophene, 40.5 g (0.3 mole) of N-methylformanilide, and 46 g (0.3 mole) of phosphoryl chloride. Two layers formed toward the end of the reaction: the upper layer was light-colored, and the lower layer was brown. The following fractions were obtained:

Fraction I, b.p. 115-117° (30 mm); 35.6 g of original 2,5-di-tert-butylthiophene
Fraction II, b.p. 117-132° (30 mm); 1.1 g
Fraction III, b.p. 132-141° (10 mm); 12.4 g
Residue 1.6 g

Fraction III was refractionated at 10 mm:

Fraction I, b.p. 132-141°; 1.94 g
Fraction II, b.p. 144-145.5°; 8.2 g (36%, on the amount of 2,5-di-tert-butylthiophene that reacted); n_D^{20} 1.5368; d_4^{20} 1.0139; found MR 69.08; calculated MR 68.57.

Found %: C 69.43, 69.46; H 8.86, 9.02; S 14.15, 14.28. $C_{13}H_{20}OS$. Calculated %: C 69.61; H 8.99; S 14.27.

After three recrystallizations from aqueous alcohol, the oxime of the aldehyde melted at 131-132°

Found %: N 5.68, 5.75. $C_{13}H_{21}OS$. Calculated %: N 5.86.

5-tert-Butyl-2-methyl- or 2-tert-Butyl-5-methyl-3-thiophenecarboxaldehyde. Formylation was carried out at 55-60°, the reactants being 26 g (0.17 mole) of 2-tert-butyl-5-methylthiophene, 27 g (0.2 mole) of N-methylformanilide, and 30.6 g (0.2 mole) of phosphoryl chloride. From the residue from ether recovery, 29 g of bisulfite compound was prepared. This was decomposed, and fractionation then gave:

Fraction I, b.p. 96° (4 mm); 0.3 g; n_D^{20} 1.5350
Fraction II, b.p. 96-97° (4 mm); 9.2 g; n_D^{20} 1.5350
Residue 0.4 g

Found %: C 66.04, 65.92; H 7.88, 7.77; S 17.60. $C_{10}H_{14}OS$. Calculated %: C 65.89; H 7.74; S 17.59.

For Fraction II d_4^{20} 1.0553; found MR 54.48; calculated MR 54.25. After being recrystallized from alcohol, the semicarbazone of this aldehyde melted at 215.5-217°.

Found %: N 17.60, 17.61. $C_{10}H_{15}NOS$. Calculated %: N 17.60.

Preparation of Nonyl Alcohol. A solution of 11 g (0.065 mole) of 5-butyl-2-thiophenecarboxaldehyde in 700 ml of 96% ethanol was prepared in a flask fitted with mercury-sealed stirrer and reflux condenser. It was heated to 60°, and 50 g of Raney nickel was added. The mixture was boiled and stirred for one hour. When the mixture was cool, the catalyst was filtered off and washed repeatedly with hot alcohol. Alcohol was distilled off, the residue was cooled, and 150 ml of water was added. The upper layer was separated, and the lower, aqueous layer was extracted with chloroform. The organic layer was combined with the chloroform extracts and dried over magnesium sulfate. Chloroform was distilled off, and vacuum distillation (14 mm) of the residue gave:

Fraction I, b.p. 137-138°, 5.14 g (yield 65%)
Residue 0.9 g

After refractionation the product still boiled at 137-138°, and it had n_D^{20} 1.4335; d_4^{20} 0.8305; found MR 45.22; calculated MR 45.29.

Found %: C 74.98, 75.10; H 13.92, 13.92. $C_9H_{20}O$. Calculated %: C 75.24; H 13.97.

After being recrystallized from 95% alcohol, the phenylurethan prepared from Fraction I melted at 59.5-60°.

Found %: N 5.56, 5.54. $C_{16}H_{25}O_2N$. Calculated %: N 5.52.

A mixture of this with the phenylurethan prepared from an authentic sample melted at 61-62°. For this urethan the literature [20] gives m.p. 62.

Preparation of 5-Decanol. A mixture prepared by the method indicated from 35 g of Raney nickel and 7 g (0.033 mole) of 5-methyl-2-thienyl 2-thienyl ketone in 350 ml of alcohol was vacuum-fractionated and gave the fractions:

Fraction I, b.p. 90-101° (26 mm); 0.6 g
Fraction II, b.p. 101-102° (25 mm); 2.9 g

When refractionated, Fraction II came over at 111-113° and had n_D^{27} 1.4312; n_D^{20} 1.4335; d_4^{20} 0.82766; found MR 49.73; calculated MR 49.90.

Found %: C 75.65, 76.03; H 14.15, 14.26. $C_{10}H_{22}O$. Calculated %: C 75.87; H 14.01.

After being recrystallized from hexane and alcohol, the 1-naphthylurethan melted at 57-58°.

Found %: N 4.38, 4.51. $C_{21}H_{29}O_2N$. Calculated %: N 4.28.

According to the literature [16], 5-decanol has the following constants: b.p. 118-120° (30 mm); n_D^{27} 1.4321. The reported melting point of its 1-naphthylurethan is 56°.

Preparation of Undecyl Alcohol. A solution of 2.9 g (0.012 mole) of 5-(5-methyl-2-thenyl)-2-thiophenecarboxaldehyde in 200 ml of ethanol was boiled with 15 g of Raney nickel. Fractionation of the reaction product gave the following fractions:

Fraction I, b.p. to 130° (15 mm); 0.1 g
Fraction II, b.p. 130-131° (15 mm); 1.24 g
Residue 0.2 g

Fractions I and II had identical constants: n_D^{23} 1.4400; d_4^{20} 0.8368; found MR 54.27; calculated MR 54.52; yield 64%.

Found %: C 76.47, 76.33; H 13.79, 13.64. $C_{11}H_{24}O$. Calculated %: C 76.67; H 14.03.

After being recrystallized from alcohol, the phenylurethan prepared from Fraction II melted at 61-62° and showed no depression when melted in admixture with the phenylurethan prepared from an authentic sample of undecyl alcohol.

Found %: N 4.79. $C_{23}H_{29}O_2N$. Calculated %: N 4.80.

According to the literature [21], undecyl alcohol boils at 147° (25 mm) and gives a phenylurethan of m.p. 62°.

Preparation of 6,6-Dimethyl-1-heptanol. A solution of 7 g (0.041 mole) of 5-tert-butyl-2-thiophenecarboxaldehyde in 350 ml of ethanol was boiled with 35 g of Raney nickel for four hours. Distillation of the product gave 3.6 g of liquid of b.p. 86-88° (12 mm). When refractionated, the product boiled at the same temperature: n_D^{20} 1.4430; d_4^{20} 0.8439; found MR 45.32; calculated MR 45.28.

Found %: C 74.65; H 13.76. $C_9H_{20}O$. Calculated %: C 74.91; H 13.67.

Preparation of 5,5-Dimethyl-2-neopentyl-1-hexanol. A mixture of 7.8 g (0.031 mole) of 2,5-di-tert-butyl-3-thiophenecarboxaldehyde, 400 ml of ethanol, and 40 g of Raney nickel was boiled for five hours. Vacuum fractionation of the product gave a few drops of liquid boiling up to 125-126° (27 mm) and 4 g (58%) of liquid of b.p. 125-126° (27 mm). Refractionation did not affect the boiling point. The liquid had n_D^{20} 1.4488; d_4^{20} 0.84705; found MR 63.42; calculated MR 63.76.

Found %: C 77.97, 77.69; H 14.20, 14.08. $C_{13}H_{28}O$. Calculated %: C 77.92; H 14.08.

The naphthylurethan was prepared from the distilled alcohol and was recrystallized from hexane and alcohol; it then melted at 110.5-112°.

Found %: N 4.26, 4.23. $C_{34}H_{35}O_2N$. Calculated %: 3.78.

Action of Raney Nickel on 5-tert-Butyl-2-methyl- or 2-tert-Butyl-5-methyl-3-thiophenecarboxaldehyde. The product obtained from 5.5 g of the aldehyde, 400 ml of ethanol, and 55 g of Raney nickel was vacuum-distilled (13 mm) and came over at 92-93°, 3.1 g being obtained. Refractionation did not affect the boiling point: n_D^{20} 1.4350; d_4^{20} 0.8386; found MR 49.57; calculated MR 49.90.

Found %: C 75.75, 75.84; H 14.18, 14.03. $C_{10}H_{22}O$. Calculated %: C 75.86; H 14.07.

After being recrystallized from hexane and 70% alcohol, the phenylurethan prepared from this alcohol melted at 62-63°.

Found %: N 4.25, 4.33. $C_{21}H_{29}O_2$. Calculated %: N 4.28.

SUMMARY

1. The following thiophene derivatives were prepared: 5-methyl-2-thienyl 2-thienyl ketone, 5-methyl-2,2'-methylenedithiophene, 5-(5-methyl-2-thenyl)-2-thiophenecarboxaldehyde, 5-butyl-2-thiophenecarboxaldehyde, 5-tert-butyl-2-methyl- or 2-tert-butyl-5-methyl-3-thiophenecarboxaldehyde, 2,5-di-tert-butyl-3-thiophenecarboxaldehyde.

2. By the action of Raney nickel of 5-methyl-2-thienyl 2-thienyl ketone, 5-(5-methyl-2-thenyl)-2-thiophenecarboxaldehyde, 5-butyl-2-thiophenecarboxaldehyde, 5-tert-butyl-2-methyl- or 2-tert-butyl-5-methyl-3-thiophenecarboxaldehyde, 2,5-di-tert-butyl-3-thiophenecarboxaldehyde, and 5-tert-butyl-2-thiophenecarboxaldehyde we were able to prepare the following aliphatic alcohols: 5-decanol, 1-undecanol, 1-nonanol, 5,5-dimethyl-2-ethyl-1-hexanol (or 4,4-dimethyl-2-propyl-1-pentanol), 5,5-dimethyl-2-neopentyl-1-hexanol, and 6,6-dimethyl-1-heptanol.

3. An attempt to bring about the hydrogenolysis of 2,5-di-tert-butyl-3-thienyl methyl ketone over Raney nickel W-5 did not give the desired results.

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*T.p. = C. B. Translation pagination.

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PHYSICAL PROPERTIES OF SOME ISODURENE HOMOLOGS

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There are no reliable data in the literature on the physical properties of homologs of isodurene [1,2,3,5-tetramethylbenzene]. Even for the closest homolog of isodurene, ethylmesitylene, the available information is very contradictory, as can be seen from Table 1. There can be no doubt that the preparations were of low purity, and only for one of them (No. 13) can the results be regarded as more or less reliable. For this preparation the freezing point was determined, and the authors [13] consider that the purity of their sample was not less than 97.5%. Unfortunately, however, the density of this comparatively pure sample was determined in a rather crude fashion – on the Westphal balance, accurate only within 0.001 g/cc. The constants of the next homolog, propylmesitylene, are given in only two papers, which appeared more than fifty years ago (b.p. 220-221°; d^{20} 0.8773 [2]; b.p. 221°; d_4^{25} 0.8757; n_D^{25} 1.5009 [14]), and these papers give no data that would permit an estimate of the purity of the preparations.

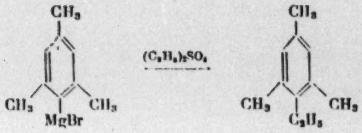
TABLE 1

Constants of Ethylmesitylene (Data from the Literature)

Preparation No.	B.p. in °C (p in mm)	M.p. (°C)	d_4^t	n_D^{20}	Literature ref.
1	212—214	Does not solidify at −20°	—	—	[1]
2	207—209	Ditto	—	—	[2]
3	208—210	—	—	—	[3]
4	93—94(16) 207—208(755)	—	0.8907 at 18.5°	1.5091 at 18.5°	[4]
5	212—214	—	—	—	[5]
6	210.2(753)	—	0,886 at 20°	1.5111	[6]
7	—	—	—	1.51167	[7]
8	210(725)	−15.56	0.894 (d_{20}^{20})	1.5074	[8]
9	208—210	—	—	—	[9]
10	207—209(750)	—	—	—	[10]
11	95—96(18)	—	—	1.5071 at 19°	[11]
12	212,4(760)	−15.5	0,883 at 20°	1.5074	[12]
13	88.5(11.8) 107.0(28) 210.2(760)	−12.2	0.888 at 18°	1.5101	[13]

In the course of work proceeding in our laboratory on the synthesis of aromatic hydrocarbons for use in a study of their Raman Spectra [15], we have synthesized the above-mentioned isodurene homologs and also allylmesitylene. As we established the degree of purity of our preparations, it was possible to determine the constants of these hydrocarbons with some precision. We therefore considered it desirable to publish our values for these constants and to give details of the synthesis and purification of our preparations.

Ethylmesitylene was prepared by Smith and Kiess's method [8], a Grignard reagent prepared from bromomesitylene being treated with diethyl sulfate:



Propylmesitylene was prepared similarly, but propyl p-toluene sulfonate was used instead of diethyl sulfate. In the preparation of allylmesitylene, allyl chloride was brought into reaction with the Grignard reagent.

In the synthesis of these hydrocarbons, measures were taken with the object of obtaining them in as pure a form as possible, not only the hydrocarbons themselves being purified carefully, but also the bromomesitylene that served as starting material for all three syntheses. The course of the purification was checked by freezing point determinations. As a result, the purified preparations contained only 0.3-1.1 mole % of impurities. The physical properties of the substances obtained are given in Table 2.

TABLE 2

Physical Properties of the Substances Prepared in this Investigation

	B.p. in °C (p in mm)	Freezing point (°C)	n_D^{20}	n_D^{25}	d_4^{20}	d_4^{25}	Cryoscopic const. (mole fraction/°C)	Purity from cooling curve (mole %)
R = Br	115.0(25)	+1.5	1.5527	—	1.3220	—	0.020	99.4
R = C_3H_5	99.3(20)	—12.1	1.5103	1.5080	0.8859	0.8824	0.017	99.7
R = C_3H_7	100.2(11.7)	—20.5	1.5052	1.5029	0.8782	0.8744	0.021	99.7
R = C_3H_5	105.5(16)	—2.1*	1.5194	—	0.8989	—	0.023	98.9

* In one of our previous papers on the study of Raman Spectra [15], as a result of a misprint, the freezing point was given incorrectly as 2.1°.

A comparison of our data with those in the literature permits us to conclude that most of the previously described preparations of ethylmesitylene were indeed highly contaminated; even the preparation cited in the latest edition of Rossini's book [12] contained about 6 mole % of impurities. On the other hand, the preparation obtained by Buck and coworkers [13] was, according to its freezing point, even purer than the authors claimed; in any case, its degree of purity was not less than 99.2%. As would be expected, the constants they gave are very similar to ours. The data in the literature on propylmesitylene are inadequate for comparison purposes. We are the first to prepare allylmesitylene, and its constants have not been given previously in the literature.

EXPERIMENTAL

Bromomesitylene. We prepared bromomesitylene by the bromination of mesitylene (890 g) in carbon tetrachloride at low temperature [16] in 80% yield. The final purification of the bromomesitylene was effected by two recrystallizations from ether at −30°; the constants of the product are given in Table 2. Its cooling curve is shown in Fig. 1. The values given in the literature for the constants of bromomesitylene refer to products of much lower purity.

Ethylmesitylene. A solution of 155 g (0.77 mole) of bromomesitylene and 11.1 g (0.10 mole) of ethyl bromide in 780 ml of absolute ether was added with stirring to 21.2 g (0.88 g-atom) of magnesium in an atmosphere of nitrogen (the reaction was first initiated with a small amount of ethyl bromide), and the mixture was heated for two hours in a water bath. A solution of 240 g (1.55 moles) of diethyl sulfate in 155 ml of absolute ether was

then added to the stirred mixture at 10°, and stirring was continued until the precipitate formed became thick. On the next day, after decomposition with 1 : 1 hydrochloric acid, the ether layer was separated, washed with water, and dried with calcium chloride. The residue remaining after removal of ether was heated with sodium ethoxide, and the hydrocarbon was extracted with ether. Ether was distilled off, and the residue was vacuum-distilled. The hydrocarbon isolated was crystallized from ether at about −60° and was then subjected to chromatography on silica gel. The head fraction contained an appreciable amount of bromomesitylene and was rejected. The main fraction (54.2 g) was vacuum-distilled through a column having an efficiency of about 50 theoretical plates.* The results of the fractionation of ethylmesitylene are given in Table 3 and Fig. 2.

Fractions VII, VIII, and IX were combined and again crystallized from ether. The resulting ethylmesitylene had the constants given in Table 2. Its cooling curve is given in Fig. 1.

TABLE 3
Results of the Fractionation of Ethylmesitylene

Fraction	B.p. (°C at 20 mm)	Yield (g)	n_D^{20}	d_4^{20}
I	62.3—99.1	4.4	1.5050	0.8756
II	99.1—99.3	4.1	1.5103	0.8856
III*	99.3	7.1	1.5103	0.8859
IV	99.3	4.4	1.5103	0.8860
V	99.3	4.5	1.5104	0.8860
VI**	99.3	4.4	1.5103	0.8860
VII	99.3	4.4	1.5103	0.8859
VIII	99.3	6.1	1.5103	0.8859
IX**	99.3	5.3	1.5103	0.8859
X	99.3—101.7	2.4	1.5104	0.8877
XI	101.7—108.2	1.0	1.5180	—
Residue		4.2	1.5480	—
Losses		1.9		

* Freezing point 12.35°.
** Freezing point 12.2°.

TABLE 4
Results of the Fractionation of Propylmesitylene

Fraction	B.p. (°C at 11.7 mm)	Yield (g)	n_D^{20}	d_4^{20}
I	98.7—100.2	2.9	1.5053	0.8788
II	100.2	2.2	1.5053	0.8782
III	100.2	4.5	1.5052	0.8782
IV	100.2	16.0	1.5052	0.8782
V	100.2	8.1	1.5052	0.8782
VI	100.2—100.7	4.1	1.5052	0.8782
Losses		1		

Propylmesitylene. In an atmosphere of nitrogen, a solution of 100 g (0.47 mole) of propyl p-toluenesulfonate** in an equal volume of ether was added to a stirred cooled solution of mesitylmagnesium bromide prepared from

* Propyl- and allyl-mesitylenes were fractionated through the same column.
** Propyl p-toluenesulfonate (b.p. 158° (6 mm); n_D^{20} 1.5074) was prepared by Izmailsky and Razorenov's method [17] and purified by Gilman's method [18].

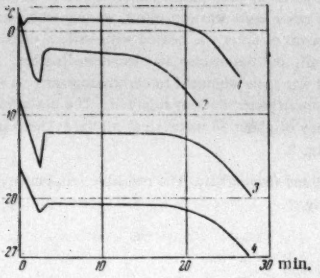


Fig. 1. Cooling curves: 1) bromomesitylene; 2) allylmesitylene; 3) ethylmesitylene; 4) propylmesitylene.

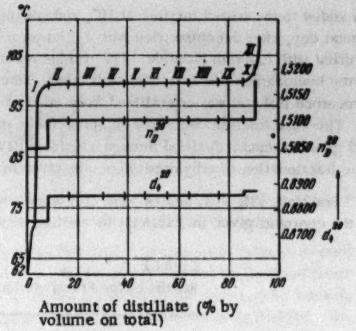


Fig. 2. Fractionation curve for ethylmesitylene.

TABLE 5

Fraction	B.p. (°C at 16 mm)	Yield (g)	n_D^{20}	d_4^{20}	Freezing point (°C)
I	59.0—104.0	4.2	1.5122	0.8912	
II	104.0—105.0	4.0	1.5227	0.9283	
III	105.0—105.1	4.8	1.5200	0.9160	
IV	105.1—105.5	5.8	1.5196	0.9025	—4.8
V	105.5	8.4	1.5194	0.8997	—3.2
VI	105.5	8.7	1.5194	0.8995	—2.9
VII	105.5	4.4	1.5193	0.8995	—3.0
Residue		1.7			
Losses		2.4			

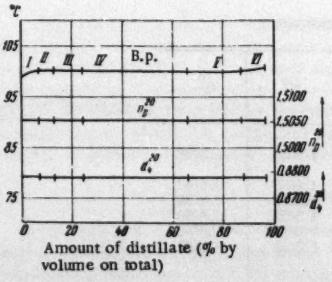


Fig. 3. Fractionation curve for propylmesitylene.

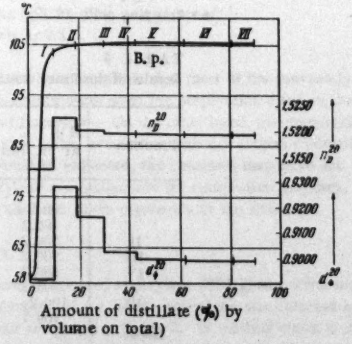


Fig. 4. Fractionation curve for allylmesitylene.

99 g (0.48 mole) of bromomesitylene, 14 g (0.58 g-atom) of magnesium, and 7 g (0.06 mole) of ethyl bromide in 350 ml of absolute ether. The reaction mixture was then heated for three hours. On the next day, after the decomposition treatment with ice and 1 : 1 hydrochloric acid, the ether layer was separated, washed with water, and

dried with calcium chloride. Ether was distilled off, and the residue was vacuum-fractionated, the fraction (49 g) boiling within the range 104-130° (39.5 mm) being collected. In all, 130 g of this fraction was obtained in the course of several parallel experiments, and this was then heated with magnesium in ether containing a little ethyl bromide, the object being the removal of residual bromomesitylene. After decomposition of the Grignard reagent and the usual treatment, the hydrocarbon still gave a positive test for bromine, and the purification treatment was repeated, after which a Beilstein test was negative. Part (38.8 g) of the propylmesitylene was then fractionated through a column. The fractionation results are given in Table 4 and Fig. 3. The constants of pure propylmesitylene are given in Table 2, and its cooling curve is given in Fig. 1.

Allylmesitylene. A solution of 76.5 g (1 mole) of allyl chloride in 50 ml of absolute ether was added at 15° to a solution of mesitylmagnesium bromide prepared from 199 g (1 mole) of bromomesitylene (with an addition of 14 g (0.13 mole) of ethyl bromide) and 30 g (1.2 g-atoms) of magnesium in 500 ml of absolute ether. The mixture was stirred at room temperature for a further two hours. On the next day, after decomposition with ice water acidified with acetic acid, the ether layer was separated, washed with water, and dried with calcium chloride. The residue remaining after removal of ether was vacuum-distilled, the fraction (74.4 g) of b.p. 113-136° (68 mm) being collected. Purification from unchanged bromomesitylene was carried out as in the case of propylmesitylene, but the allylmesitylene gave a negative Beilstein test already after the first treatment. A part (44.4 g) of the allylmesitylene was vacuum-fractionated through a column. The results of the fractionation are given in Table 5 and Fig. 4.

Fraction VI was recrystallized from ether at low temperature. The constants of the preparation obtained are given in Table 2, and the cooling curve is shown in Fig. 1. Analysis gave the following results:

Found %: C 89.86, 89.76; H 10.11, 10.03. $C_{12}H_{16}$. Calculated %: C 89.93; H 10.07.

SUMMARY

1. Highly pure (above 99.5%) samples of ethyl- and propyl-mesitylenes were synthesized, and their constants were determined.

2. A sample of about 99% purity of previously undescribed allylmesitylene was synthesized.

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EFFICIENCIES OF VARIOUS CATALYSTS IN THE ALKYLATION OF BENZENE WITH PROPENE

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The alkylation reaction has attracted the attention of chemists for a very long time [1]. As benzene homologs have found wide application in industry, interest in this reaction increases with every year. Among the alkylbenzenes that have already found application, particular mention may be made of isopropylbenzene, which is prepared in the petroleum industry as a component of aviation gasoline. In recent years alkylbenzenes have begun to be applied mainly as raw material for the chemical industry in the manufacture of styrene, methylstyrene, phenol, acetone, dicarboxylic acids, synthetic detergents, etc. The field of application of the alkylation of benzene is shown diagrammatically in Fig. 1.

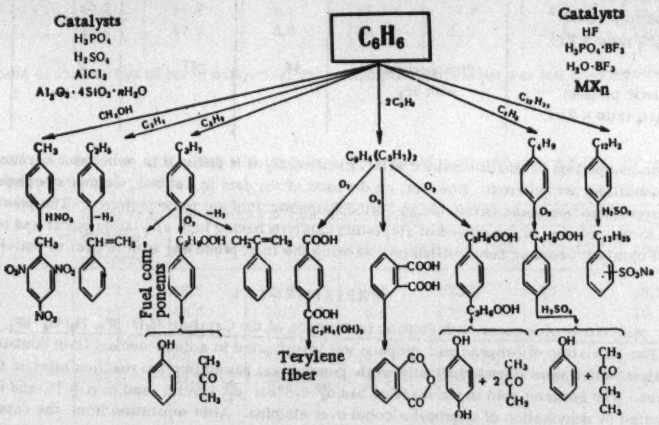

Fig. 1. Field of application of the alkylation of benzene.

The catalysts mainly used at present for the alkylation of benzene with olefins are sulfuric acid, phosphoric acid, aluminum chloride, aluminosilicates, hydrogen fluoride, and the compounds formed by boron trifluoride with water and phosphoric acid [2-7]. More rarely, zinc chloride and other such halides find application [8-10].

The catalysts vary in catalytic activity, and their specificity in the alkylation of benzene with olefins manifests itself in the yield of monoalkylbenzenes, the yield of di- and poly-alkylbenzenes, the formation of polymers, the optimum molar ratio of benzene to olefin, and the volume of the reaction space and ancillary apparatus.

All this, taken as a whole, determines the efficiency of the alkylation process, so that the correct choice of catalyst is of great importance, particularly when we consider the scale on which various alkylbenzenes are manufactured – it attains tens and hundreds of thousands of tons per year. Of the catalysts mentioned above, only phos-

phoric acid (on kieselguhr), sulfuric acid, aluminum chloride, and hydrogen fluoride have as yet found industrial application. Characteristics of processes of alkylation of benzene with propene over various catalysts are given in Table 1.

TABLE 1

Characteristics of Various Processes of Alkylation of Benzene with a Propane-Propene Fraction

Conditions of process	Catalyst	Composition of mixture (%)			Yield (%) of isopropylbenzene
		benzene	alkylbenzene	polyalkylbenzene	
Temperature 15-20° Excess pressure 10 atm $C_6H_6 : C_3H_6$ ratio = 2:1	Sulfuric acid	40	40	20	50
Temperature 180-20° Excess pressure 15-20 atm $C_6H_6 : C_3H_6$ ratio = 10	Phosphoric acid on kieselguhr	46.3	43.4	10.3	58
Temperature 350° Excess pressure 20 atm $C_6H_6 : C_3H_6$ ratio = 5:1	Aluminosilicate				
Temperature 20° Excess pressure 10 atm $C_6H_6 : C_3H_6$ ratio = 2:1	Hydrofluoric acid	46.3	43.4	10.3	58
Temperature 50° Atmospheric pressure $C_6H_6 : C_3H_6$ ratio = 2:1	Aluminum chloride	45	43	12	46
Temperature 50° Atmospheric pressure $C_6H_6 : C_3H_6$ ratio = 2:1	Phosphoric acid with BF_3	44	47	9	76

The comparison of results obtained with various catalysts is difficult in some cases because the experimental conditions are different. However, on the basis of the data in Table 1, we may conclude tentatively that catalysts based on boron trifluoride and orthophosphoric acid are to be preferred. The present paper is devoted to the question of the choice of alkylation catalysts having high alkylating power and to the investigation of catalysts based on boron trifluoride, as being the most promising with respect to activity.

EXPERIMENTAL

1. Alkylation of Benzene with Propene in Presence of the Catalysts $H_2O \cdot BF_3$, $H_3PO_4 \cdot BF_3$, H_2SO_4 and $AlCl_3$. The alkylation of benzene with propene was investigated in a three-necked flask containing benzene and catalyst, which were stirred vigorously while propene was passed into the reaction mixture through a capillary tube. The benzene used in the reaction had d_4^{20} 0.8784; n_D^{20} 1.5010; and m.p. 5.1°, and the propene was prepared by dehydration of isopropyl alcohol over alumina. After separation from the catalyst (and in the case of $AlCl_3 \cdot HSO_4$ and $AlCl_3$, after the decomposition of the catalyst with water), the reaction products were washed, dried, and fractionated from a flask with a column into a benzene fraction, b.p. 80-120°, and a monoalkyl fraction, b.p. 120-170°. The residue, the fraction boiling above 170°, was a mixture of mono-, di-, tri-, and tetraisopropylbenzenes. Also, the monoalkyl fraction (fraction boiling above 120°) was fractionated through a 15-plate column. It was found that the diisopropylbenzene, which was made use of in the reaction in some cases, consisted of the ortho and para isomers.

The catalysts $H_2O \cdot BF_3$ and $H_3PO_4 \cdot BF_3$ were prepared by saturating water and phosphoric acid, respectively, with boron trifluoride in accordance with the usual method [11]. Physical properties of catalysts based on boron trifluoride are given in Table 2.

In Table 3, we give the results of the alkylation of benzene with propene in presence of various catalysts at 50°; 156 g of benzene and 42 g of propene were taken in all cases.

TABLE 2

Characteristics of Catalysts Based on Boron Trifluoride at 20°

Catalyst	Boron trifluoride content		Density	Viscosity (centistokes)	Conductivity ($ohm^{-1}cm^{-1}$)
	found	calculated			
$H_3PO_4 \cdot BF_3$	40.5	40.9	1.9030	43.08	0.00583
88.7% $H_3PO_4 \cdot BF_3$	52.0	51.0	1.8784	16.96	0.01025
$H_2O \cdot BF_3$	78.1	79.0	1.7793	–	0.03507

TABLE 3

Yield of Alkylbenzene Upon Alkylyzation of Benzene with Propene in Presence of Various Catalysts (Molar Ratio of $C_6H_6 : C_3H_6 = 2:1$)

Catalyst	Composition of hydrocarbon layer (%)			Yield of fraction (%)			Consumption of catalyst (%)
	up to 120°	120-170°	above 170°	120-170°	152-153°	above 170°	
$H_3PO_4 \cdot BF_3$	42.0	53.0	5.0	88.0	82.0	8.3	2.9•
88.7% $H_3PO_4 \cdot BF_3$	41.8	53.6	4.6	88.4	82.8	7.6	3.3
$AlCl_3$	46.2	39.2	14.6	64.2	57.7	26.2	10.0
$AlCl_3 \cdot HSO_4$	45.8	32.2	22.0	53.2	49.0	36.3	15.0
$H_2O \cdot BF_3$	40.2	56.8	2.5	93.3	87.8	4.2	15.4
H_2SO_4	43.6	47.6	8.8	78.6	71.1	14.5	22.0

•Under conditions excluding loss of boron trifluoride, the consumption of catalyst was less than 1%.

TABLE 4

Characteristics of the Alkylation of Benzene with Propene in Presence of $H_3PO_4 \cdot BF_3$ and $AlCl_3$ at 50° with Various Benzene : Propene Molar Ratios

Catalyst	Molar ratio benzene : : propene	Composition of hydrocarbon layer			Yield of reaction products (%)		
		up to 120°	120-170°	above 170°	120-170°	152-153°	above 170°
$AlCl_3$	2:1	46.2	39.2	14.6	64.2	57.7	26.2
$AlCl_3$	4:1	68.7	25.7	5.6	75.3	63.3	16.5
$H_3PO_4 \cdot BF_3$	1.5:1	32.0	55.0	13.3	73.0	63.3	17.2
$H_3PO_4 \cdot BF_3$	2:1	42.0	53.0	5.0	88.0	79.0	8.3
$H_3PO_4 \cdot BF_3$	4:1	67.6	29.2	3.2	90.0	79.1	4.0

Values of the consumptions of six catalysts in the alkylation of benzene with propene, as given in Table 3, show that the most efficient catalysts for this reaction are compounds of boron trifluoride with orthophosphoric acid, which are superior to aluminum chloride. A comparison of the action of aluminum chloride with that of the complex formed between orthophosphoric acid and boron trifluoride in the alkylation of benzene with propene for various molar ratios of the reactants (Table 4) confirms our conclusion concerning the high alkylating power of the complex $H_3PO_4 \cdot BF_3$. Thus, similar yields of isopropylbenzene are obtained with $H_3PO_4 \cdot BF_3$ (69.3%) and $AlCl_3$ (63.3%) for benzene : propene molar ratios of 1.5 : 1 and 4 : 1, respectively.

Fractionation curves for the monoalkyl fraction (b.p. above 120°) are given in Fig. 2.

Under comparable experimental conditions, the highest concentration of isopropylbenzene is obtained by the use of catalysts based on boron trifluoride. The results of the investigation show that this catalyst has considerable advantages over aluminum chloride and sulfuric acid, for it increases the yield of isopropylbenzene, while at the same time depressing the formation of polyisopropylbenzenes. The specific action of the catalyst affects the composition of the reaction product, for thermodynamic equilibrium is not attained during the time taken by the reaction. If it were attained, then all catalysts would give the same result as far as the composition of the product is concerned.

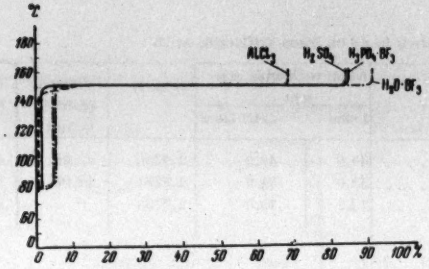

Fig. 2. Fractionation of fractions of b.p. above 120° obtained with different catalysts.

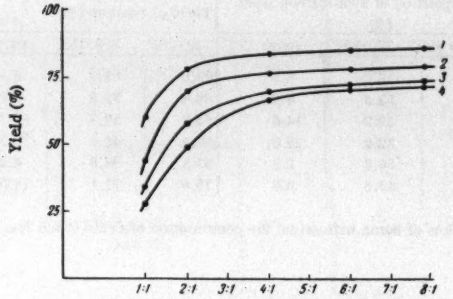

Fig. 3. Dependence of the yield of isopropylbenzene (fraction of b.p. 152-153°) on the molar ratio benzene: propene in the alkylation of benzene with propene in presence of various catalysts: 1) $H_3PO_4 \cdot BF_3$; 2) H_2SO_4; 3) $AlCl_3$; 4) $AlCl_3 \cdot H_2SO_4$.

Investigation of the alkylation of benzene with propene in presence of various catalysts with various molar ratios of benzene to propene shows that over the whole range investigated the yield of isopropylbenzene is greatest with a catalyst based on boron trifluoride. The results of the experiments are shown graphically in Fig. 3.

2. The Effects of Various Factors on the Alkylation of Benzene with Propene in Presence of 88.7% of $H_3PO_4 \cdot BF_3$. We studied the effects of various factors on the alkylation of benzene with propene in presence of the catalyst obtained by saturation of the usual 88.7% orthophosphoric acid with boron trifluoride. The composition of the catalyst can be represented as follows: 11.3% $H_2O \cdot BF_3$ + 88.7% $H_3PO_4 \cdot BF_3$. It is actually a solution of $H_2O \cdot BF_3$ in $H_3PO_4 \cdot BF_3$.

As will be seen from these results, as the amount of catalyst taking part in the reaction increases, the yield of isopropylbenzene increases. Thus, when 5% of catalyst is taken, the yield is 71.8%, whereas for 35% of catalyst the yield is already 84.5%. In this case the increase in yield is more than 12%.

The effect of reaction temperature is very marked when it is raised from 20° to 50° (see Table 5). The optimum temperature for the alkylation of benzene with propene in presence of the complex formed between orthophosphoric acid and boron trifluoride is 50°, for further rise in temperature has practically no effect on the yield of isopropylbenzene, but increases the rate at which the catalyst is exhausted. The yield and composition

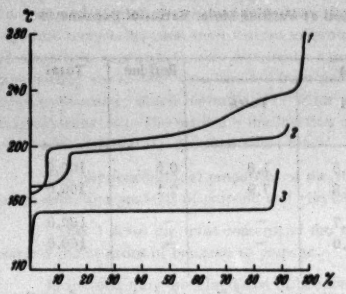

Fig. 4. Fractionation of alkylated benzene: 1) Fraction of b.p. above 170° ($C_6H_6 : C_3H_6 = 1:1$); 2) Fraction of b.p. above 170° ($C_6H_6 : C_3H_6 = 2:1$); 3) Fraction of b.p. 120-170°.

of the alkylation products is affected appreciably by change in the molar ratio of benzene to propene. Results of an investigation into the effect of variation of the molar ratio of the reactants from 1:1 to 8:1 are given in Table 6.

A favorable condition for this reaction is the use of a large excess of benzene, which helps to suppress reactions of secondary alkylation and polymerization. Whereas a molar ratio of benzene to propene of 1:1 gave a 68.0% yield of the 120-170° fraction and a 32% yield of the fraction boiling above 170°, at a ratio of 8:1 the yields were 92.4% and 7.4%, respectively.

With the object of determining the amounts of the various alkylbenzenes in the reaction product, the latter was fractionated through a 20-plate column. First a fraction boiling up to 120° was collected, then a fraction of b.p. 120-170°, and finally a fraction boiling above 170°. The corresponding fractions from identical experiments were combined and refractionated together with definite amounts of alkylbenzenes of various degress of substitution. Typical fractionation results are shown in Fig. 4. The alkylation product obtained at a 2:1 molar ratio of benzene to propene contained 83.2% of isopropylbenzene, 4.0% of intermediate fractions, consisting of mixtures of benzene, isopropylbenzene, and diisopropylbenzene, and also 12.4% of a fraction that was almost pure diisopropylbenzene. The results were rendered more precise by taking the molecular weights of the intermediate fractions into account, and it was found that the hydrocarbon layer obtained after reaction consisted of 42.84% of benzene and 57.16% of alkylation products. Under the experimental conditions no polymerization of propene was observed.

TABLE 5

Effects of the Amount of Catalyst and of the Reaction Temperature on the Yield and Composition of the Reaction Products in the Alkylation of Benzene with Propene (molar ratio $C_6H_6 : C_3H_6 = 2:1$).

Temperature, °C	Amount of catalyst (% on benzene)	Yield of isopropylbenzene (152-153° fraction (%)	Composition of reaction product (% by weight)		
			up to 120°	120-170°	above 170°
20	15	74.0	43.0	47.3	8.9
50	15	78.0	42.3	49.6	7.3
80	15	78.2	42.0	50.0	7.0
50	5	71.8	43.0	46.5	9.5
50	25	81.0	41.3	51.5	6.1
50	35	84.5	41.8	52.6	5.0

TABLE 6

Alkylation of Benzene with Propene at Various Molar Ratios of Benzene to Propene

Molar ratio benzene : propene	Yield of fraction (%)			Composition of reaction product (% by weight)		
	120-170°	152-153°	above 170°	up to 120°	120-170°	above 170°
1:1	68.0	67.0	32.0	9.9	68.1	21.5
2:1	82.0	78.0	18.0	42.3	49.6	7.3
4:1	88.0	84.0	12.0	66.7	29.8	2.7
6:1	91.4	85.5	8.6	76.2	21.6	1.3
8:1	92.4	86.0	7.4	81.4	16.6	0.9

TABLE 7

Contents of Various Alkylbenzenes in Alkylation Products Obtained at Various Molar Ratios of Benzene to Propene

Molar ratio benzene : propene	Product	Isopropylbenzenes (%)				Residue	Total
		Mono	Di	Tri	Tetra		
1:1	Monoalkyl fraction	77.1	13.1	7.5	1.8	0.5	100.0
	Polyalkyl fraction	–	57.2	32.8	7.9	2.1	100.0
2:1	Monoalkyl fraction	90.0	9.3	0.7	–	–	100.0
	Polyalkyl fraction	–	93.0	7.0	–	–	100.0

The diisopropylbenzene fraction, b.p. above 170°, was investigated carefully. As can be seen from the fractionation curve (Fig. 4), 72% comes over in the temperature ranges 194-200° and 200-207°, and the curve then has an inflection and gradually rises. This form of curve indicates that the mixture being distilled probably consisted of various isomers of diisopropylbenzene. In order to determine the amounts of the isomers formed more exactly, the 194-200° and 200-207° fractions were collected together and refractionated. The following fractions were obtained:

Fraction I	b.p. 192-202°	1.2%
Fraction II	b.p. 202-204°	90.0%
Fraction III	b.p. 204-207°	2.3%
Fraction IV	b.p. above 207°	6.5%

When adequate amounts of the fractions had been collected, the one-degree fractions of b.p. 203-204° and 210-211° were isolated from them. Fraction of b.p. 203-204° had d_4^{20} 0.8695; n_D^{20} 1.4905; found MR 54.08; calculated MR 54.02; Fraction of b.p. 210-211° had d_4^{20} 0.8565; n_D^{20} 1.4898; found MR 54.51; calculated MR 54.02.

In order to determine the positions of the alkyl groups the fractions were oxidized with potassium permanganate in an alkaline medium. As a result of the oxidation of the fraction of b.p. 203-204° and repeated boiling of the product with water, insoluble crystals, m.p. 300°, were isolated in a yield of 75% on the total amount of acids produced. Oxidation of the fraction of b.p. 210-211° also gave water-insoluble crystals, m.p. 300°, the yield being 99%. The acids so obtained were converted into the dimethyl ester, which melted at 140°. It may be considered to be proved that the dicarboxylic acid was terephthalic acid.

TABLE 8

Effect of Different Catalysts on Yield and Composition of Diisopropylbenzene Fraction (50° $C_6H_6 : C_3H_6 = 2:1$)

Catalyst	Yield of polyisopropylbenzenes (%)	Diisopropylbenzene content of the polyisopropylbenzene fraction (%)	p-Diisopropylbenzene content of the diisopropylbenzene fraction (%)
$AlCl_3$	35	60	30
$AlCl_2 \cdot HSO_4$	54	58	70
H_2SO_4	20	70	75
$H_3PO_4 \cdot BF_3$	10	93	78
$H_2O \cdot BF_3$	6	93	80

The aqueous extracts of the products of the oxidation of the fraction of b.p. 203-204° yielded 25% of white crystals, m.p. 190°, undepressed by admixture of phthalic acid. These crystals therefore consisted of phthalic acid. The amounts of the acids isolated and the relative amounts of the respective fractions indicate that the diisopropylbenzene fraction consisted of 78% of p-diisopropylbenzene and 22% of o-diisopropylbenzene.

From the alkylation product obtained at a molar ratio of benzene to propene of 1:1, a fraction of b.p. 235-237° was isolated; after purification with sulfuric acid, this fraction had the following constants: b.p. 236-237.5°; d_4^{20} 0.8588; n_D^{20} 1.4912; bromine value 0; molecular weight 202.

In order to determine the structures of the triisopropylbenzenes formed in the alkylation of benzene with

propene, the fraction of b.p. 236-237.5° was oxidized with potassium permanganate in an alkaline medium. Oxidation of 18 g of the triisopropylbenzene fraction resulted in the isolation of 10 g of acids, from which, by repeated recrystallization from various solvents (water, ethanol, acetone), 15% of trimesic acid (1,3,5) and 85% of trimellitic acid (1,2,4) were obtained. Also, a tetraisopropylbenzene fraction of b.p. 234-280° and a fraction boiling above 280° were isolated from the alkylation product. The first fraction contained 80% of tetraisopropylbenzene, which melted at 117° after recrystallization from ethanol; this corresponds to 1,2,4,5-tetraisopropylbenzene. The residue - the fraction of b.p. above 280° - was an oily liquid, d_4^{20} 0.8690; n_D^{20} 1.5020; molecular weight 341; bromine value 3.5.

The physicochemical properties of the residue indicate that it consisted of a mixture of hydrodehydropolymerization products of propene and alkylbenzenes.

Table 7 shows the total contents of the various isopropylbenzenes in the alkylation products obtained at various molar ratios of benzene to propene.

In investigating the alkylation of benzene with propene in presence of various catalysts, we paid particular attention to the diisopropylbenzene fraction. We determined the p-diisopropylbenzene content of this fraction. The results are given in Table 8.

It follows from this that catalysts based on boron trifluoride and sulfuric acid direct the isopropyl group largely into the para position.

3. Retardation of the Formation of Polyalkylbenzenes in the Alkylation of Benzene with Propene in Presence of Aluminum Chloride. The alkylation of benzene with propene in presence of aluminum chloride can be regarded as a coupled equilibrium process of alkylation and dealkylation:

$$C_6H_6 + C_3H_6 = xC_6H_5C_3H_7 + yC_6H_4(C_3H_7)_2.$$

TABLE 9

Alkylation of Benzene with Propene in Presence of Added Polyisopropylbenzenes at 50°

Experiment	Reactants and their amounts*	Yield of reaction products (% on propene)			Productivity of reaction space
		Isopropylbenzene 145-160°	Alkylation product 190-270°	Polyisopropylbenzene fraction, b.p. above 280°	alkylation product, kg / reactor volume, liter
1	C_6H_6 — 2.0 C_3H_6 — 1.0 $AlCl_3$ — 15	145	181.2	75.6	0.378
2	C_6H_6 — 4.0 C_3H_6 — 1.0 $AlCl_3$ — 15	177	208	50.0	0.218
3	C_6H_6 — 1.75 C_3H_6 — 1.0 $AlCl_3$ — 15	165	209.8	40.2	0.440
4	C_6H_6 — 1.5 C_3H_6 — 1.0 $AlCl_3$ — 15 $C_{12}H_{18}$ — 0.5	161	221	18.9	0.464
5	C_6H_6 — 1.35 C_3H_6 — 1.0 $C_{12}H_{18}$ — 0.85 $AlCl_3$ — 15	214.4	227.5	61.6	0.476
6	C_6H_6 — 1.1 C_3H_6 — 1.0 $C_{12}H_{18}$ — 0.9 $AlCl_3$ — 15	—	228.7	—13.2	0.480
7	C_6H_6 — 3.0 C_3H_6 — 1.0 $C_{12}H_{18}$ — 1.0 $AlCl_3$ — 15	214	285.9	—46.6	0.316

*Hydrocarbons - in moles; $AlCl_3$ - in percentage; $C_{12}H_{18}$, i.e., diisopropylbenzene - amount expressed as number of moles of benzene replaced by an equivalent amount by weight of $C_{12}H_{18}$.

It would appear that the relative amounts of isopropyl- and diisopropyl-benzenes are determined by the

equilibrium conditions, which depend mainly on the excess of benzene taken for reaction. It was thought that a preliminary addition of diisopropylbenzene to the reaction mixture would displace the equilibrium and hinder the formation of polyisopropylbenzenes from benzene and propene, so that the whole of the propene taken would be used for the formation of the monoalkylbenzene.

For the reaction we took 31-42 g of propene, 117-176 g of benzene, 20-60 g of polyisopropylbenzene, and 15% on the weight of the reaction mixture of commerical aluminum chloride. Propene was passed in from a gas holder at the rate of 1.5-2 liters per hour. The treatment of the reaction mixture was as before. Table 9 gives the results of experiments on the alkylation of benzene with propene at molar ratios $C_6H_6 : C_3H_6$ of 2:1 and 4:1, part of the benzene being replaced by polyisopropylbenzenes in some of the experiments. Experiments 1 and 2 in Table 9 show the effect of molar excess of benzene over propene on the yield of alkylation product (fraction of b.p. 120-170°) and of isopropylbenzene (fraction of b.p. 145-160°): they increase with increase in the amount of benzene.

Increase in the benzene : propene ratio, though resulting in an increased yield of monoalkylbenzene, makes it necessary to distill off a large amount of benzene in order to isolate the alkylation product. As can be seen from the last column of Table 9, the productivity of the reaction space with respect to alkylation product is lowered from 0.379 to 0.218. It follows from Experiments 3-6 that the replacement of 0.25, 0.5, 0.65, and 0.9 mole of benzene by polyisopropylbenzenes results in an increase in the yield of alkylation product from 181% to 228% and in an increase in the yield of isopropylbenzene from 145% to 214%, without change in the volume of the reaction mixture. At the same time, the productivity of the reaction space is increased from 0.379 to 0.46 kg of alkylation product per liter of useful reaction space.

These experiments show that alkylation of benzene with propene with addition of polyisopropylbenzenes to the reaction mixture may be carried out without appreciable formation of polyisopropylbenzenes, if the relative amounts of benzene, polyisopropylbenzenes, and aluminum chloride are suitably chosen. New polyisopropylbenzene is not formed, or is formed in only very small amount, and the added polyisopropylbenzene is recirculated in the process. The addition of polyisopropylbenzenes in the alkylation of benzene with propene in presence of acid catalysts such as H_2SO_4 and $H_3PO_4 \cdot BF_3$ does not result in increase in the yield of monoisopropylbenzene.

SUMMARY

1. The alkylation of benzene with propene in presence of $H_2O \cdot BF_3$, $H_3PO_4 \cdot BF_3$, $H_3PO_4 \cdot BF_3 - H_2O \cdot BF_3$, $AlCl_3$, H_2SO_4, and $AlCl_3 \cdot HSO_4$ was investigated at atmospheric pressure under given experimental conditions, account being taken of the molar ratio of the reacting hydrocarbons, the temperature, and the amount of catalyst. The superiority of the catalyst $H_3PO_4 \cdot BF_3$ was demonstrated.

2. In the alkylation of benzene with propene in presence of aluminum chloride, the formation of polyisopropylbenzenes may be effectively prevented by addition of polyisopropylbenzenes to the reaction mixture. In alkylation in presence of acid catalysts such as H_2SO_4 and $H_3PO_4 \cdot BF_3$, addition of polyisopropylbenzenes is not effective, for the reaction does not attain an equilibrium state.

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QUANTITATIVE INVESTIGATION OF STERIC HINDRANCE

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The concept of steric hindrance, as an inhibitory effect arising in a reaction from the shielding of the reaction center by ramified structures in other parts of the molecule, was developed in its general form during the nineties of the last century [1], but there followed a period of more than forty years in which no further progress was made toward a more precise formulation of the concept. A glance into the past will enable us to understand the cause of this long delay. Steric hindrance is associated with reaction rates: it is a kinetic, not thermodynamic phenomenon, and it therefore depends on reaction mechanism. For this reason, the operation of steric hindrance could not be described precisely until the various possible reaction mechanisms had been determined and adequately characterized.

Much of the necessary information on reaction mechanisms was collected during the thirties of this century, and it became clear that any given reaction of a general type may proceed by different mechanisms and that the mechanism by which it will actually proceed will depend both on the structures of the reactants and on the reaction conditions - including, in particular, the electrochemical properties of the solvent. It was established that steric factors may have greatly differing effects on different reaction mechanisms, and it became clear also that steric factors affecting reaction rate are very directly associated with the geometry of transition states (which had not been elucidated at that time), and not only with the well established geometry of normal molecules, on which all previous attempts to explain steric hindrance had been based.

By 1940 our picture of the operation of steric hindrance had become clear [2]: the effect is determined partly by reaction mechanism and partly by molecular structure. Its most important feature, which we shall now discuss, is associated with mechanism.

It has been shown that, in the main, the mechanisms of the principal types of investigated organic reactions fall into two classes, termed "unimolecular" and "bimolecular" respectively. The first of these is characterized by a reaction rate determined by a dissociation process, whereas for the second the determining process is associative in type. These two types of mechanisms tend to be grouped symmetrically. Thus, for nucleophilic substitution two mechanisms are possible, one of each type; the hydrolysis of carboxylic esters can proceed by six mechanisms, three of each type; and so on. Whatever the reaction may be, however, steric effects influence the two different types of mechanisms in substantially different ways. Unimolecular reactions are determined kinetically by dissociation, so that in the formation of the transition state the mean density of matter in the neighborhood of the reaction center must diminish and there must be local reduction in the value of some previously existing internal pressure. Even when we take into account the possible effect of geometric changes due to the formation of the transition state, it is nevertheless found that, owing to the general diminution in the density of matter, there can be no appreciable overall increase in pressure - or, more exactly, in potential energy due to pressure. Correspondingly, in the case of unimolecular mechanisms, steric factors can bring about some acceleration of reaction, but not any great retardation. In the case of bimolecular mechanisms, reaction rate is determined by an association process in which there is an increase in the density of matter near the reaction center in the transition state. It follows that bimolecular reactions may be greatly retarded under the influence of steric factors.

On the basis of this view concerning the main feature in our picture of the operation of kinetic steric efforts, we undertook exploratory work, mainly of a somewhat simplified and qualitative character, with the object of determining more completely the distinctive characteristics of this picture. This work still continues.

In the course of these investigations it was found that, apart from the general distinction associated with the character of the mechanism, there are finer, though appreciable, differences associated with the type of

molecular structure. The structure of a molecule directly determines its geometry in the proximity of the reaction center in its original state, whereas the corresponding geometry of the transition state is determined both by the structure of the molecule and by the mechanism of the reaction. For a given mechanism, therefore, the structural type of the substrate determines the change in geometry associated with the change from the initial to the transition state, and so determines also the increase or reduction in internal pressure due to the kinetic steric effect. For example, the reaction of nucleophilic substitution corresponds essentially to one unimolecular and one bimolecular mechanism. In the unimolecular mechanism, the changes in geometry are different in the alkyl, aryl, and aralkyl series. These differences enable us to understand why, in the first two cases, groups in the immediate vicinity can cause a small acceleration [3,4], which may be explained by the occurrence of an overall reduction of pressure in the formation of a transition state of the dissociative type. In the third case a slight retardation is observed [5] when the change in geometry results in an additional pressure which more than compensates for the lowering of pressure peculiar to dissociative process. In just the same way, in the bimolecular mechanism the kinetically important changes in geometry are not the same in the alkyl, aryl, and aralkyl series [5-7]; and when we take these differences into account, we can understand why the retardation of reaction attributable to steric hindrance - which is observed in all three series - is so much greater in the first series than in the other two.

This exploratory work is still continuing, for even when we confine ourselves to the fundamentally most important reactions, possible mechanisms, and structural types, the number of combinations deserving attention still remains very great. Investigations in such a wide field must necessarily have a somewhat superficial and qualitative character, but this stage of the work is essential for the selection of individual topics for more profound study, such as the topic discussed in this paper. Generally speaking, there is no reason why any of the fair variety of fields covered by this exploratory work should be left without a more intensive, quantitative investigation. As yet, however, very few topics have been so treated. A more profound investigation of this sort has been carried out during the last decade (1945-55) in parallel with the further development of the above-mentioned extensive, but superficial, investigations.

The topic selected for investigation was nucleophilic substitution in alkyl compounds by the bimolecular mechanism - the reaction of S_N2 aliphatic substitution, as we shall refer to it for the sake of brevity. Long before the start of this work, a crude analysis of the appropriate geometric relationships led to some unexpected conclusions [7]. These conclusions were very surprising in that, although they were arrived at by a rigorous treatment, from the point of view of the old intuitive approach they were absurd. One of these conclusions was that in S_N2 aliphatic substitutions steric hindrance may increase as the point of substitution recedes from the ramified part of the molecule, as, for example, when we pass from a tert-butyl halide to a neopentyl halide - a view that is in conflict with Victor Meyer's results on the esterification of ortho-substituted benzoic and phenylacetic acids. Another conclusion was that, although, steric hindrance should depend greatly on the shape of the alkyl group, it should be almost independent of the size of the incoming group; a large group should enter a confined space just as readily as a smaller group. Although these conclusions were published, it can scarcely be said that their validity was at all widely accepted. Later, however, they were confirmed experimentally, and their quantitative aspects were elucidated theoretically. These investigations revealed still other such phenomena, which were also found to be capable of rational explanation. Properly speaking, these phenomena should have been foreseen, though, as a matter of fact, they were not. We shall refer to them in the appropriate places.

The example selected for our study of substitution [8] was the Finkelstein reaction

$$Y^- + RX \rightarrow RY - X^-,$$

in which X and Y are isotopically or chemically different halogens, and R is an alkyl group. The solvent used was acetone, for it has suitable solvent properties for various combinations of halogens; moreover, for alkyl groups varying greatly in structure, reaction in this solvent proceeds exclusively, or almost exclusively, by the bimolecular mechanism.

In investigations of this kind we have to work simultaneously along two directions - theoretical and experimental - basing our strategy on the concurrence found between the results of these two lines of work, and advancing, as it were, by a pincer movement.

We shall first discuss the results of our experimental observations, the extent of which can be judged from the data on reaction rates given in Table 1. Seven of the possible nine Finkelstein exchange reactions

with chlorine, bromine, and iodine were investigated for the seven alkyl groups comprising the simplest members of the α- and the β-methylated series of branching homologs.

According to the Arrhenius equation, the rate constant of a reaction can be expressed, in principle, as the product of two factors: $k = Be^{-E/RT}$, or $\log k = \log B - E/4.575\,T$. The frequency factor B, otherwise called the entropy factor, is multiplied by the energy factor $\exp(-E/RT)$, which depends on the activation energy E. The most immediate experimental problem is therefore the resolution of each rate constant into its component factors. This resolution is based on the well known fact that only the energy factor is explicitly dependent on temperature.

Any examination that we may make of the effect of structure on any property capable of undergoing change can be only a relative one: we can consider only the effect of changes in structure. Hence, in order to examine the effect of structural peculiarities on the rate constant and on its component factors, we must select a suitable structure as standard. Suitable standards for these reactions are the methyl derivatives, and we shall examine the changes in the experimental values of the two factors in the expression for the rate constant by comparison with this standard.

TABLE 1

Finkelstein S_N2 Exchange Reactions in Acetone for the α-Methylated Branching Homologous Alkyls CH_3, C_2H_5, i-C_3H_7, t-C_4H_9 and the β-Methylated Branching Homologous Alkyls C_2H_5, n-C_3H_7, i-C_4H_9, neo-C_5H_{11} (Values of $10^5 \cdot k_2$ at 25° in liter · sec^{-1} $mole^{-1}$).

Reactants	CH_3	C_2H_5	i-C_3H_7	t-C_4H_9	n-C_3H_7	i-C_4H_9	neo-C_5H_{11}
$Cl^- + RCl$ . . .	3.9	0.050	—	—	—	—	—
$Cl^- + RBr$ . . .	600	9.9	0.13	0.029	6.4	1.5	0.00026
$Cl^- + RI$ . . .	470	42	1.3	—	25	1.6	0.00058
$Br^- + RBr$ . . .	13 000	170	1.8	0.51	110	5.7	0.0026
$Br^- + RI$ . . .	27 000	1490	37	—	1050	32	—
$I^- + RBr$ . . .	25 000	170	1.3	0.10	140	6.0	0.0020
$I^- + RI$ . . .	—	6000	53	18	—	—	0.11

As regards the energy factor, the procedure adopted is to subtract the activation energy for the methyl derivative from that for the derivative under consideration. In this way we obtain the values given in Table 2 for the excess of activation energy ΔE. These values give a measure of the effect of structure on activation energy, i.e., they represent an effect that is amenable to theoretical discussion.

TABLE 2

Observed Increments in Activation Energy ΔE for Finkelstein S_N2 Exchange Reactions (in acetone as solvent)*

Reactants	CH_3	C_2H_5	i-C_3H_7	t-C_4H_9	n-C_3H_7	i-C_4H_9	neo-C_5H_{11}
$Cl^- + RCl$ . . .	0.0	1.3	—	—	—	—	—
$Cl^- + RBr$ . . .	0.0	1.9	2.9	5.3	2.1	2.6	6.0
$Cl^- + RI$ . . .	0.0	1.2	1.6	—	1.4	1.8	6.0
$Br^- + RBr$ . . .	0.0	1.7	3.9	6.0	1.7	3.1	6.2
$Br^- + RI$ . . .	0.0	1.4	2.2	—	1.6	2.5	6.9
$I^- + RBr$ . . .	0.0	2.6	4.2	6.9	2.7	3.6	7.9
$I^- + RI$ . . .	0.0	1.7	3.7	5.7	—	—	6.5

*All values are in kcal/mole.

It will be seen from Table 2 that no general tendency can be observed in the changes of ΔE as we pass from the smaller halogen atoms to the larger: there is only an irregular scatter. On the other hand, as we pass from one alkyl group to another, notable changes in activation energy are observed: there is a general increase in the α-methylated series (CH_3, C_2H_5, i-C_3H_7, t-C_4H_9), and there is an increase, at first scarcely appreciable and then more rapid, in the β-methylated series (C_2H_5, n-C_3H_7, i-C_4H_9, neo-C_5H_{11}). The activation energy is somewhat higher for neo-C_5H_{11} than for t-C_4H_9.

For an analogous examination of the frequency factor, values of log B for the methyl derivatives are subtracted from values for each of the given reactions so that we obtain a series of experimental differences that we call increments, although they are all negative except a few which have a value of zero. They are given in Table 3 and they reflect the effect of structure on the logarithm of the frequency factor, or what amounts to the same, if we neglect the change in scale, on the activation entropy. These quantities are also amenable to theoretical discussion.

TABLE 3

Observed Increments in the Logarithm of the Frequency Factor Δ log B for Finkelstein S_N2 Exchange Reactions (in acetone as solvent).

Reactants	CH_3	C_2H_5	i-C_3H_7	t-C_4H_9	n-C_5H_{11}	i-C_5H_{11}	neo-C_5H_{11}
Cl^-+RCl . . .	0.0	—0.8	—	—	—	—	—
Cl^-+RBr . . .	0.0	—0.4	—1.4	—0.4	—0.7	—0.9	—1.9
Cl^-+RI . . .	0.0	—0.3	—1.1	—	—0.6	—1.1	—1.5
Br^-+RBr . . .	0.0	—0.6	—1.0	±0.0	—0.9	—1.1	—2.1
Br^-+RI . . .	0.0	—0.3	—1.2	—	—0.6	—1.1	—1.3
I^- + RBr . . .	0.0	—0.4	—1.2	—0.3	—0.6	—1.1	—1.2
I^- + RI . . .	0.0	—0.5	—1.0	±0.0	—	—	—1.8

Here also we can observe some general regularities: 1) as we pass from the smaller halogen atoms to the larger, no general tendency is to be observed, only a certain scatter; 2) in the replacement of alkyl groups the changes occurring are striking and uniform. For the first three members of the α-methylated series (CH_3, C_2H_5, i-C_3H_7) the values of Δ log B gradually fall, but then return, or almost return, to their original values at the fourth member (t-C_4H_9). In the β-methylated series (C_2H_5, n-C_3H_7, i-C_4H_9, neo-C_5H_{11}) Δ log B falls in a regular fashion. For neo-C_5H_{11} the frequency factors are thus less than for t-C_4H_9.

Such are the results which the purely experimental development of the problem has contributed to the investigation.

The theoretical treatment of the problem is based on the model of the transition state that has been established for S_N2 alkyl-substitution reactions. In this model, semi-ionic semi-bonds, holding the groups that are substituting and being substituted in the transition state, are disposed on the two sides of a plane containing three bonds originally having a pyramidal configuration, which must undergo inversion in the course of the reaction. This, of course, is a general, qualitative model: at this stage it does not convey the exact configuration of any concrete transition state.

Hence, the main problem in the preliminary stage of the theoretical investigation of the effect of structural factors on the kinetics of any of the reactions under consideration consists in calculations for several configurations of atoms which may be regarded as close to the arrangement in the transition state, the object being to determine the energies required to build up all these configurations from the original reactants. For each assumed configuration it is necessary to calculate the energy required for the stretching of the carbon-halogen bond to a certain distance between the atoms, the energy required to cause a halide ion to approach an α-carbon atom to a given distance, the energy required for the bending of certain bonds, and so on. All these energies must then be added together in order to give the total energy necessary for the formation of a given configuration, expressed as a function of this configuration. If an intelligent choice of configurations is made, the energy will have a minimum value for a certain configuration, which will correspond to the transi-

tion state. If we use the graphical method, we may say that we are constructing an "energy surface", and the spatial and energy coordinates of the lowest point of this surface corresponds to the configuration and energy of the transition state. Such calculations must be carried out for each individual reaction, i.e. for each combination of halogens and alkyl group.

The only mathematical equipment required consists of three approximate, but well verified, formulas of the simplest possible type: a formula for bond-stretching, a formula for bond bending, and a formula for non-bonding compression potentials. All the constants in these formulas are either universal constants, or are determined by known values of certain mechanical, thermal, and optical properties of standard substances. No auxiliary parameters are introduced at any stage in the construction of these energy surfaces.

TABLE 4

Calculated Positions of Iodine in Transition States of the Reaction $I^- + RI \rightarrow IR + I^-$

R	Extra length of each semi bond $C_{...}I$ (A)	Angle at which $I_{...}C_{...}I$ bond is bent
CH_3	0.36	0.0°
C_2H_5	0.37	3.8°
$i\text{-}C_3H_7$	0.38	5.0°
$t\text{-}C_4H_9$	0.40	0.0°
$n\text{-}C_4H_7$	0.37	3.8°
$i\text{-}C_4H_9$	0.39	5.0°
$neo\text{-}C_5H_{11}$	0.43	17.6°

The simplest application of these surfaces consists in the determination of the configurations and energies of transition states. As an illustration of calculated configurations of transition states, in Table 4 we give the positions of iodine in the transition states of reactions of isotopic exchange of iodine, these being expressed by the lengths and angles of the carbon-iodine bonds. In the transition states, all the carbon-halogen bonds are stretched, some to a greater and others to a lesser extent owing to the differences in the pressures of the different alkyl groups. With the exception of transition states containing methyl and tert-butyl groups, which have trigonal symmetry with respect to strictly linear halogen-carbon-halogen bonds, in all cases the carbon-halogen bonds are bent; in the transition states containing neopentyl groups, these bonds are very severely bent.

In Table 5 we give the calculated differences between the energy of the transition state containing the methyl group and the energies of the transition states containing the other groups, i.e., the calculated increments of activation energy due to steric effects ΔW_{ster} for three reactions of exchange between identical halogens. As will be seen from the table, as we pass from the smaller halogen atoms to the larger, the calculated steric increments of energy change only slightly and not always in the way that would be expected on the basis of the usual intuitive approach: for example, some of the values fall. However, as the alkyl groups are changed, there is a marked regular change in the energy increments, which rise in the α-methylated series, but remain constant at first in the β-methylated series and then rise at an increasing rate. The relationship between these calculated values are in accord not only with earlier qualitative predictions, but also with basic laws governing these activation energies which were discovered subsequently by experiment.

TABLE 5

Calculated Steric Increments of Energy ΔW_{ster} (kcal/mole) for S_N2 Finkelstein Substitutions

	CH_3	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	$n\text{-}C_4H_7$	$i\text{-}C_4H_9$	$neo\text{-}C_5H_{11}$
$Cl^- + RCl$ . .	0.0	0.8	1.6	2.8	0.8	2.1	6.5
$Br^- + RBr$ . . .	0.0	0.8	1.6	2.5	0.8	2.3	7.3
$I^- + RI$ . . .	0.0	0.7	1.3	2.0	0.7	2.5	7.8

The calculated quantities are steric increments of activation energy ΔW_{ster}. We do not yet possess a suitable method for the calculation of the fraction of the activation energy due to polarity ΔW_{pol} on the basis of simple assumptions. We can make a further step forward, therefore, only by comparing experimental values of ΔE with calculated values of ΔW_{ster} and determining whether the differences between these quantities, which may be considered to be the ΔW_{pol} component, correspond to the actual picture of the polar effect. It was found that there is indeed a correspondence in two important respects: 1) the differences found can be as-

sociated exclusively with α-alkyl substitution, but in the case of β-alkyl substitution there is no appreciable variation in the differences, which is the behavior to be expected when there is a weak polar effect in a non-conducting system (for a steric effect such a distribution would be incorrect); 2) the differences are governed, approximately, by an additive free energy equation, as is generally observed for polar effects isolated from steric effects. These two simplifying relationships, and also the close electrochemical similarities between the halogens, enable us to assume a single round value of 1.0 kcal per mole for the polar effect of an α-alkyl substituent in any alkyl group in any Finkelstein exchange reaction, thus enabling us to calculate all 49 values of ΔW_{pol}.

In general, the sum of ΔW_{ster} and ΔW_{pol} is very close to the experimental value of ΔE, although the agreement is only approximate in the case of the neopentyl group. The less satisfactory agreement in this case may be explained by the fact that the calculation of ΔW_{ster} for neopentyl is associated with large errors, and high calculated values may be expected. As an illustration of the numerical values found, data for the bromine-exchange reaction are given in Table 6. A more general but equally good illustration is provided by the closeness and absence of trend in both calculated and experimental values for the replacement of one halogen by another; this will be seen from the comparison made in the table between the average calculated values for all of the reactions investigated and the mean experimental values.

Another way of using the calculated energy surfaces consists in finding the frequency factor in the expression for the reaction-rate constant. The logarithm of the frequency factor is the activation entropy, if we leave out of account possible (or arbitrary) changes in the origin and the units of entropy; the entropy of the transition state is greatly dependent on these energy surfaces - and on their geometric form rather than on their energy level.

In the general case, every surface has the form of a basket. To use a figurative comparison, we may say that the reagent and the group being removed can be regarded as participants in a game of basketball, in which an "energy basket" is used. The lower and the wider the basket, the more frequently will molecules fall into it with formation of the transition state. The height of the basket, which represents energy, has been already considered. We shall now consider its width, which represents entropy.

TABLE 6

Calculated and Experimental Effects of Alkyl Structure in Finkelstein S_N2 Exchange Reactions on Activation Energies (kcal mole)

	CH_3	H_5C_5	i-C_3H_7	t-C_4H_9	n-C_5H_7	i-C_4H_9	neo-C_5H_{11}
			Reaction $Br^- + RBr \rightarrow BrR + Br^-$				
ΔW_{ster}	0	0.8	1.6	2.5	0.8	2.3	7.3
ΔW_{pol}	0	1.0	2.0	3.0	1.0	1.0	1.0
ΔE_{calc}	0	1.8	3.6	5.5	1.8	3.3	8.3
ΔE_{expt}	0	1.7	3.9	6.0	1.7	3.1	6.2
Difference	0	+0.1	−0.3	−0.5	+0.1	+0.2	+2.1
			Means for all reactions investigated				
ΔW_{ster}	0	0.8	1.5	2.4	0.8	2.3	7.2
ΔW_{pol}	0	1.0	2.0	3.0	1.0	1.0	1.0
ΔE_{calc}	0	1.8	3.5	5.4	1.8	3.3	8.2
ΔE_{expt}	0	1.7	3.1	6.0	1.9	2.7	6.6
Difference	0	+0.4	+0.4	−0.6	−0.1	+0.6	+1.6

Basketlike surfaces of this sort are shown in Fig. 1 for four alkyl groups in the bromine-exchange reaction. The groups are selected so as to illustrate the peculiar character of the effect of steric conditions on the frequency factor in the expression for the reaction-rate constant: the sign of the effect is essentially determined by symmetry.

These contour diagrams clearly reflect the fact that for the tert-butyl group the transition state preserves the axial symmetry of the transition state of the methyl group, whereas for the ethyl and neopentyl groups the transition states are characterized by increasing departure from this symmetry. It must here be pointed out

that for the tert-butyl group the basket is wider than for the methyl group, particularly in the axial direction (along the axis of abscissae), whereas the baskets for the ethyl and neopentyl groups become increasingly narrow, particularly in the transverse direction. The reason for the greater width of the tert-butyl basket lies in the fact that steric pressure is here directed outwards and the forces in the bonds, which are in a stretched condition, are weakened; as a result, the energy gradients will be less steep and the basket will become shallower and more open. In this particular instance, there is no side pressure or force tending to bend the bonds which could compensate for this effect by means of pressure on the sides of the basket. In the case of the ethyl group, however, and still more in the case of the neopentyl group, steric pressure directed from the sides is the dominant effect. Hence, this pressure acts on the basket from one side, and a bending potential acts from the other, so that the walls of the basket become steeper and the basket itself becomes narrower. It can be seen, therefore, that, depending on its direction, steric pressure may have either an accelerating or retarding effect on the frequency factor. From the point of view of the usual intuitive approach, the part played by the direction distribution of this effect is an absurd one, since steric interaction that directly repels the reagent acts as an accelerator of reaction, and interaction tending to direct the reagent sideways acts as a retardant.

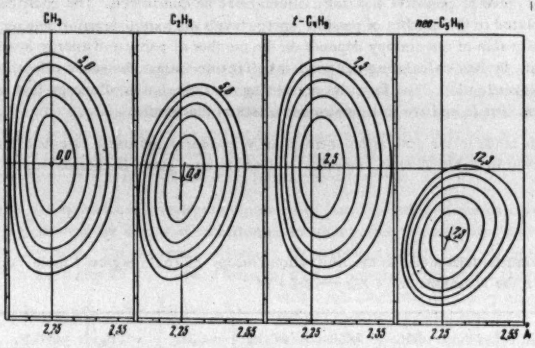

Fig. 1. Calculated energy surfaces for the reaction $Br^- + RBr \rightarrow BrR + Br^-$. Four basket-shaped surfaces for R = CH_3, C_2H_5, t-C_4H_9 and neo-C_5H_{11}. The figures against the contours are energies (kcal/mole) reckoned from the lowest point of the methyl surface as zero. The horizontal axis is a line passing through C-α perpendicular to the plane of the three intact C-α bonds in the transition state. The intersection of the axes of coordinates corresponds to the positions which, according to calculation, the halogen atoms would have in absence of steric hindrance, and the points are the calculated positions of the halogen atoms in presence of steric hindrance. The relative heights of the bottoms of the baskets correspond to the contribution made by steric factors to the activation energy, and the relative widths of the baskets to the contribution of steric factors to the activation entropy (in all the diagrams the contours are at 1 kcal/mole intervals).

In the interest of correct "score-keeping", we must point out that this game of basketball does not proceed according to Newton's laws of mechanics, but follows quantum laws, so that we must estimate the widths of our baskets not with the aid of classical measurement, but by quantum counting. It is necessary to calculate the number of energy levels in the basket - statistically weighted according to Boltzmann - since it is this number which, according to quantum rules, determines the capacity of the basket, which we express in the form of the logarithm of the entropy.

However, as soon as we begin to calculate the capacity of the basket in this way, it is found that this capacity depends not only on the geometry of the energy surface, but also on the masses and their distribution in the particles taking part in the reaction. As is well known, a given energy well contains a greater number of energy levels in the case of a heavy particle than in the case of a light one, and moreover this increase in the number of levels represents a step toward the limit constituting an energy continuum at infinitely large mass, as required by Bohr's correspondence principle. These simple considerations result in the disclosure of a new

type of structural effect on reaction rate which has not yet been examined in sufficient detail and which is neither a steric nor a polar effect; it was called "ponderal", since it depends on mass and does not depend on how a given heavy group fills space and how any charge it may have is distributed. A purely ponderal effect should be brought about by neutrons added, as is completely feasible, to the molecule by isotopic exchange, since neutrons, while possessing mass, have neither volume nor charge.

The structural effects that affect kinetics can therefore be divided into three categories. The ponderal effect depends on the presence and distribution of masses, the steric effect on the presence and distribution of volumes, and the polar effect on the presence and distribution of charges. There can be no doubt that appreciable ponderal effects have often remained undetected when associated with steric and polar effects.

In principle, ponderal, steric, and polar effects affect both the energy, and also the entropy factor in the reaction-rate constant. In the present work, however, since we are concerned with relatively heavy particles, we may neglect – and in fact have neglected – the influence of the ponderal effect on the energy. Similarly, we may neglect the polar effect when considering the entropy term, for alkyl substituents are only weakly polar; only contributions made by ponderal and steric effects need be considered. The contribution of the ponderal effect is to be related to the number of possible energy levels when steric pressure does not deform the energy surface. The total value of the entropy depends on the number of permitted energy levels arising when the surface is deformed. By first calculating the ponderal effect we isolate the steric effect, which was the original object of our investigation. The formulas permitting the calculation of energy levels with due regard to statistical weights are simple and are well known in statistical mechanics.

The contributions made to the activation entropy ΔS by ponderal and steric effects in the bromine-exchange reaction are given in Table 7. The numerical values are here given in thermal units, not frequency units.

TABLE 7

Calculated Contributions Made to the Activation Entropy ΔS (cal · degree^{-1} mole^{-1}) by Structural Effects in the Reactions $Br^- + RBr \rightarrow BrR + Br^-$.

	CH_3	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	$n\text{-}C_5H_{11}$	$i\text{-}C_5H_9$	$neo\text{-}C_5H_{11}$
Ponderal	0.00	—1.45	—2.30	—1.95	—2.64	—3.66	—4.39
Steric	0.00	—0.66	—1.52	+0.83	—0.67	—1.06	—1.86
Total	0.00	—2.11	—3.82	—1.12	—3.31	—4.72	—6.25

With increase in mass the ponderal effect generally results in a retarding action, as indicated by the negative signs of values given in Table 7. The ponderal effect may be somewhat confused with the steric effect in these considerations in which mass has the predominating effect, but they cannot be confused in our considerations relating to another law on the distribution of masses, which is considered below. As can be seen by a comparison of isomers, extra mass generally has the greater retarding effect, the greater its distance from the reaction center. Elementary intuition might lead us to the first of the above rules, but not in any circumstances to the second. The point is that addition or removal of mass causes a greater increase in the number of energy levels in the original molecule than in the transition state. However, the actual effect of the distribution of masses is so complex that there may be exceptions to these rules.

As regards the steric entropy effect, the values obtained confirm qualitative conclusions based on the form of the energy surface. As can be seen from the fact that the positive sign occurs only once, the steric effect causes acceleration only in the case of the tert-butyl group, for which steric pressure is directed outwards; in all the other cases, in which the pressure is directed sideways, the steric effect results in retardation.

When the contributions of the individual effects are added together, it is found that the total entropy effect always leads to retardation, which is least for the tert-butyl group and greatest for neopentyl.

The relationship between entropy in thermal units and the frequency factor in the expression for the re-

action-rate constant has the form $\Delta \log B = \Delta S/4.575$; a simple change of scale therefore makes it possible to make a comparison with experiment. This comparison is given in Table 8, first for the bromine-exchange reaction, and second for mean values from all the reactions investigated.

TABLE 8

Calculated and Observed Structure Effects on log B for Bimolecular Finkelstein Exchange Reactions.

	CH_3	C_2H_5	i-C_3H_7	t-C_4H_9	n-C_5H_{11}	i-C_5H_{11}	neo-C_5H_{11}
Observed*	0.0	−0.6	−1.0	±0.0	−0.9	−1.1	−2.1
Calculated*	0.0	−0.46	−0.84	−0.24	−0.72	−1.03	−1.37
Observed (mean)	0.0	−0.5	−1.1	−0.2	−0.7	−1.1	−1.6

* (Br exchange)

It will be seen that, in general, agreement is good. In all cases, except that of the neopentyl group, agreement is within the limits of experimental error, which may attain ±0.2. Even the poorer agreement for the neopentyl group can be explained by the fact that in this case the calculation is less accurate than in the remaining cases and can result in a departure in just that direction in which it is observed. It should be noted that at no stage in these calculations of entropy were any supplementary parameters introduced: the formulas used contain only constants that have been found by independent methods.

The last step of the theoretical investigation consists in the combining of the calculated activation energies and entropy factors with the object of determining to what extent the combination corresponds to the observed reaction-rate constants. This is done in detail in the diagrams in Fig. 2, in which the vertical scales for ΔE, $\Delta \log B$, and $\Delta \log k$ (for 25°) have been selected so that corresponding points give direct indications of the relative parts played by energy and entropy in the determination of reaction rate: by subtracting the ordinate ΔE from the ordinate $\Delta \log B$, we may immediately find the ordinate $\Delta \log k$. The lines for the α-methylated series (continuous) and for the β-methylated series (broken) are theoretical and have a dual purpose: in the first place they unite calculated points for the reaction of bromine exchange, and in the second place they unite points for the mean values for all reactions; these mean points are so near to those calculated for the bromine-exchange reaction that the lines cannot be drawn separately. The crosses correspond to the observed points for bromine exchange, and the circles to the means of the observed values for all reactions. With the exception of the points for neopentyl groups, the observed values are well reproduced by the calculated ones. These calculations also enable us to understand some important features, such as the fact that in the case of the tert-butyl group the reactions are only slightly slower than in the case of the isopropyl group and the fact that for the neopentyl group reaction is much slower than for all the other groups, even the tert-butyl group.

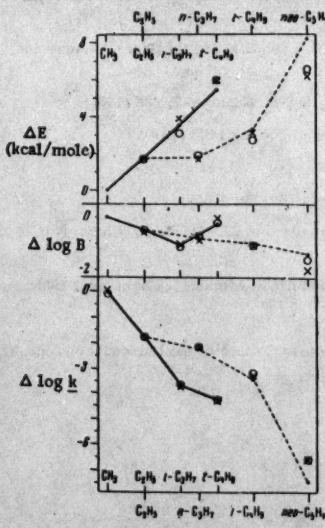

Fig. 2. Calculated and observed effects of alkyl structure on the energy and entropy rate factors and on the resulting rates of Finkelstein reactions (for explanation see text).

Table 9 gives a comparison of numerical values of observed and calculated rate constants for the bromine-exchange reaction. Most of the calculated values depart from the experimental values by a factor of less than two, although the departure is by a factor of five in the case of the neopentyl group, this being the max-

imum departure over the whole range of reaction rates, which vary by a factor of 5,000,000.

TABLE 9

Observed and Calculated Effects of Structure on the Rate Constant for 25° for the Reaction $Br^- + RBr \rightarrow BrR + Br^-$ in Acetone.

	CH_3	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	$n\text{-}C_3H_7$	$i\text{-}C_4H_9$	$neo\text{-}C_5H_{11}$
Observed	1	0.013	0.00014	0.000039	0.0085	0.00044	0.00000020
Calculated	1	0.017	0.00035	0.000053	0.0090	0.00035	0.000000037

This comparison shows to what extent the "pincer movement" carried out by the theoretical and experimental investigations has closed in this campaign for the solution of the problem we have been set. Further improvements in accuracy are possible in the application of each of these methods, but this is a very laborious task. However, since a rather approximate analysis of the effect of structure on reaction rate in a certain particular system has enabled us to reveal so many effects of general character which are not only not revealed, but are even masked in an intuitive examination, we consider that a similar approximate examination of other types of structure, of other reaction mechanisms, and of other reactions could also lead to conclusions of wide significance at which it would be impossible to arrive by any other means. Work on a similar approximate treatment of new material may therefore be of greater value than attempts to attain significantly higher accuracy.

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PRINCIPLES UNDERLYING NEW METHODS FOR THE CHEMICAL TREATMENT OF COMPLEX IRON AND NICKEL ORES

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For an economically satisfactory solution of the problem of the chemical treatment of iron-nickel oxide and oxide silicate ores, it is of primary importance that the iron, which is present in these ores in considerable amounts, should be utilized rationally. The previous extensive investigations on the hydrometallurgy of iron-nickel oxide ores [1] did not provide a satisfactory solution of this problem; the passage of iron into solution in an amount substantially greater than that of nickel led to considerable consumption of solvents, which made the proposed processes uneconomic and resulted in the loss of the whole of the extracted iron in solutions and filter cakes. Investigations carried out in various institutes over many years with the object of reducing the passage of iron into solution as much as possible did not yield the desired results: the consumption of acid reagents still remained above the acceptable limit, so that the proposed acid-leaching procedures were unsatisfactory from the economic and technological points of view.

In these earlier investigations [1] special procedures were adopted with the object of lowering the rate of extraction of iron from the ore and diminishing the consumption of reagents, but we proposed [2] to utilize the iron that must inevitably react by repeated use of iron-containing lyes and other intermediate products as cheap active reagent-solvents. This procedure greatly reduces the consumption of reagents in hydrometallurgical treatments of complex iron-nickel ores.

In the processes of greatest practical importance, namely, leaching with sulfuric acid with utilization of sulfurous gases [2,3] and chlorination [4,5], both proposed by us [2-4] for the treatment of complex iron-nickel oxide and oxide-silicate ores, the iron is extracted in the form of its sulfates and chlorides. For this reason, the greatest practical interest is presented by an investigation into the possibility of using various solutions of these iron compounds as reagent-solvents in hydrometallurgy and into the conditions required in their application. The tasks undertaken in the work carried out with this aim were 1) a study of the chemical interaction of solutions of ferric sulfate, of ferric chloride, and of mineral acids of various concentrations with typical nickel silicate minerals, with nickelous oxide, and with metallic nickel; 2) an investigation of the relation between the rates of these processes and the physicochemical conditions under which they are carried out; 3) the determination of the optimum conditions for carrying out these processes in practice in order to effect maximum transfer of valuable metals into solution; and 4) an investigation of the possibility in principle and the optimum conditions for the efficient chemical treatment of complex iron-nickel oxide and oxide-silicate ores from the principal commercially worked Soviet deposits with the recommended solvents under the conditions proposed.

EXPERIMENTAL

Materials Investigated, Experimental Procedure, and Experimental Results

The materials investigated were a) magnesium-nickel hydrosilicate minerals — Ufalei garnierite, Akkerman garnierite, Ufalei nepouite-garnierite, Akkerman nickel cerolite, and Akkerman nickel deweylite; b) nickel hydroaluminosilicate minerals — Aidyrlin nickel aluminosilicate and Aidyrlin aidyrlite; c) nickelous oxide; d) "active" metallic nickel prepared by the reduction of nickelous oxide and nickel oxide solid solutions [6] with hydrogen under the conditions previously [7, 8] found to be optimum for these processes; and e) complex iron-nickel oxide-silicate ores — Ufalei oxide-silicate ore, low-grade oxide-silicate ore from Batamshin, and waste oxide-silicate ore from Aiderbak (Khalil region).

The nickelous oxide taken for the leaching process was prepared by roasting (above 1100° to constant weight) the nickel oxide solid solution prepared by the decomposition of chemically pure nickel nitrate in the low-temperature region [8]. The oxide-silicate minerals and ores were obtained from the Museum of Geology and Mineralogy of the Academy of Sciences of the USSR and from the mining and geological sections of the Ufalei nickel works and the South Urals Nickel Combine.

In order to make a detailed physicochemical study of these minerals and ores, they were subjected to chemical, mechanical, screening, magnetic, mineralogical, differential, thermal, and densimetric investigations; also, their reducibility with various reducing agents was studied [9].

Garnierite – $(Ni, Mg)O \cdot SiO_2 \cdot H_2O$ – is the most widely distributed nickel oxide-silicate mineral. It is green and has a dull appearance; its hardness is 2-2.5; it has an even fracture – plane-conchoidal and conchoidal. Its aggregates are gellike, or sometimes ocherous. In the cold, dilute acids have almost no action, but at the boil the mineral decomposes slightly. It is decomposed by concentrated hydrochloric and sulfuric acids. The action of salt solutions on garnierite has not been studied.

Nepouite – $3(Ni, Mg)O \cdot 2SiO_2 \cdot 2H_2O$ – is a widely distributed oxide-silicate mineral of nickel, being the product of the partial replacement of magnesium oxide by nickelous oxide in serpentine. It is a distinctly crystalline mineral, probably hexagonal in form, and it generally gives small long bluish-green crystals or plates. Its hardness is 2-3 and its density 2.7-2.8. It reacts like garnierite with mineral acids. The action of salt solutions on nepouite has not been studied.

Nickel cerolite – $(Mg, Ni)O \cdot SiO_2 \cdot H_2O$ – is a gellike magnesium-nickel hydrosilicate. It is bright bluish green. It is very brittle and has a conchoidal fracture. Its hardness is 2-2.5. It will not mark paper, and it cannot be polished with the fingernail. Its aggregates are compact and gellike. In the cold, weak acids have almost no action on cerolite, and at the boil they decompose it only partially. In boiling concentrated hydrochloric and sulfuric acids cerolite is completely decomposed. The action of salt solutions on nickel cerolite has not been studied.

Nickel deweylite – $4(Mg, Ni)O \cdot 3SiO_2 \cdot 3H_2O$ – is a magnesium-nickel hydrosilicate. It is bright grass-green and varies from mat to glasslike in appearance. It is brittle and has a hardness of 2.5-3.5. Its aggregates are gellike. Weak acids have almost no action on deweylite, but boiling concentrated hydrochloric acid decomposes it. The action of salt solutions on nickel deweylite has not been studied.

Nickel aluminosilicate and aidyrlite are hydroaluminosilicates of variable composition: their chemical formulas have not been firmly established. Macroscopically, nickel aluminosilicate has the appearance of large bright-blue completely homogeneous pieces having a greasy feel, and aidyrlite is a bright greenish-blue mineral that is rather dry to the touch. Microscopically, the bulk of a sample of aidyrlite is seen to be an intimate mixture of this mineral, in the form of radiating columnar nepouite-like aggregates, with quartz. In samples of nickel aluminosilicate, none of the known nickel oxide-silicate minerals could be detected microscopically. Both aidyrlite and nickel aluminosilicate are new oxide-silicate nickel minerals, and their physicochemical properties have not yet been studied in detail.

Ufalei oxide-silicate ore is a yellowish-brown, ocherous-argillaceous mass having an indefinite schistose texture and containing fine lenslike inclusions of nontronite and well-leached chrysotile. The nonmagnetic part of the various fractions from screen analysis consists mainly of talc, quartz, nontronite, ocherous hydrogoethite, hydrohematite, and ferrihalloysite. The magnetic part of the various fractions consists of highly corroded free grains of magnetite. Most of the fine granular part of the ore consists of minerals that do not contain nickel (talc, magnetite, quartz). The nickel-bearing constituents of this ore are 1) argillaceous fractions containing adsorbed nickel compounds; 2) nontronite; 3) ferrihalloysite; and 4) ocherous hydrogoethite. Apart from extremely rare single scales of nepouite, there are no clearly individualized nickel minerals in the ore investigated. Apart from some extremely rare single inclusions of asbolan, no cobalt-bearing minerals were detected in the ore. The results of a chemical and mineralogical investigation of Ufalei ore show that this ore belongs to a type of low-grade talc-like iron-nickel oxide-silicate ores which do not contain cobalt and that it is characteristic for the ores of this type found in the Ufalei district.

Batamshin oxide-silicate ore is a dark-brown ocherous spongy mass which contains much fragmental material consisting of well-leached serpentinite that is somewhat cerolitized, nontronitzed, and opalized, and also of opal, nontronite, dolomite, and serpophite. The nonmagnetic part of the various fractions from screen analysis

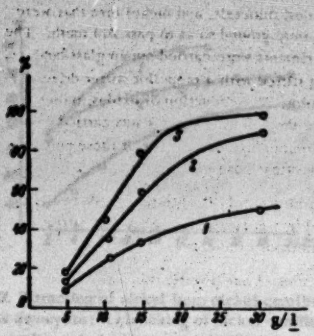

Fig. 1. Extraction of nickel from garnierite by leaching with ferric sulfate solutions, expressed as a function of the composition of the solvent and the duration of the leaching process: 1) 2 hours; 2) 4 hours; 3) 6 hours.

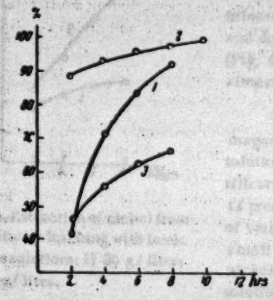

Fig. 2. Extraction of nickel from nepouite-garnierite and nickel aluminosilicate by leaching treatments: 1) leaching of nepouite-garnierite with ferric sulfate solution (65 g/liter); 2) leaching of nickel aluminosilicate with ferric sulfate solution (30 g/liter); 3) leaching of nickel aluminosilicate with sulfuric acid solution (3%).

consists mainly of hyalite, chalcedony, quartz, serpentinite, nontronite, and ocherous hydrogoethite. The magnetic part of the various fractions consists mainly of magnetite and well-leached serpentinite in admixture with other minerals. In its chemical and mineralogical composition the ore, being formed mainly from ocher and nontronitized, leached serpentinite, belongs to the type of mixed ores. The nickel, which passes mainly into the nonmagnetic fractions, is present in the ore in the form of the following minerals: 1) garnierite, containing up to 45% of nickelous oxide; 2) asbolan, containing up to 10-12% of nickelous oxide; 3) psilomelanvade, containing up to 20% of nickelous oxide; 4) nontronite, containing up to 3-5% of nickelous oxide; 5) serpentine, containing up to 1% of adsorbed nickelous oxide; 6) cerolite, containing up to 1% of adsorbed nickelous oxide; and 7) iron hydroxides, containing various amounts of adsorbed nickelous oxides. Of the nickel-containing minerals in the ore, nontronite and iron hydroxides greatly predominate in amount. The amounts of individualized nickel silicates are very slight. Owing to the insignificance of the amount of asbolan and psilomelanvades in this ore, it is a very low-grade ore from the point of view of cobalt content. The low-grade Batamshin iron-nickel oxide-silicate ore is characteristic for most deposits of this ore in the Orsko-Aktyubin district.

Aiderbak oxide-silicate ore, which belongs to the class of final decomposition products of serpentinites, is an ocherous nontronitized serpentinite having an olive-green to brown color. Most of the ore consists of nontronite, and hydrohematite is present in appreciable amount. A little fragmentary material present in the main friable mass of the ore consists principally of opal and films and dendrites of manganese oxides, highly leached nontronized serpentinite, and black manganese chalcedony. The nonmagnetic part of various fractions from screen analysis consists mainly of opal, chalcedony, nontronite, and hydrohematite. The magnetic fractions are mainly magnetite, but hydrogoethite and chrome spinelides are also present. Individualized nickel minerals are present in the ore only in extremely small amount. The nickel is finely dispersed in the ore in the form of garnierite, prasopal, and nontronite. Cobalt-containing asbolans and psilomelanvades are altogether absent. The investigated Aiderbak ore is a typical waste iron-nickel oxide-silicate ore, characteristic of the deposits of this type of ore in the Khalil district.

As planned, the nickel silicate minerals, nickelous oxide, metallic nickel, and nickel oxide-silicate ores were leached with solutions of ferric sulfate, ferric chloride, sulfuric acid, and nitric acid of various concentration. The leaching conditions were suitably varied with the object of studying the following basic questions: 1) dependance of the intensity of the leaching processes on the composition of the original solutions, on the temperature, and on the duration of the process; 2) the part played by the concentration and variation in concentration of ferric sulfate, ferric chloride, or mineral acid in leaching processes; 3) the effect of variation in the acidity of the medium in such processes; and 4) the effect of these factors on the passage of nickel into solutions in the investigated leaching processes.

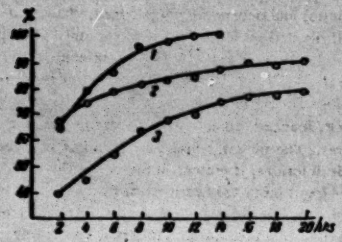

Fig. 3. Extraction of nickel from nickel cerolite and nickel deweylite: 1) leaching of nickel cerolite with ferric sulfate solution (30 g/liter); 2) leaching of nickel deweylite with ferric sulfate solution (45 g/liter); 3) leaching of nickel deweylite with ferric sulfate solution (30 g/liter).

The oxides, minerals, and nickel ores that were to be leached were ground so as to pass 200 mesh. The leaching experiments were carried out in glass beakers, the pulp being stirred with a propellor stirrer driven by an electric motor. The reduction of oxides, minerals, and ores before the leaching process was carried out under the optimum conditions found for these processes in previous investigations [9, 10].

The chemical analysis of the solutions and filter cakes obtained by the leaching process was carried out by the usual methods of analytical chemistry.

Some results of our investigations are shown in Figures 1-8. Unlike existing data in the literature [11], these experimental data show that nickelous oxide does not react sufficiently readily with ferric sulfate solutions of various concentrations, so that bunsenite cannot be adequately leached from nickel oxide ores by this method. As we have shown for the first time, in spite of contrary indications in the literature [11], much more intense reaction occurs between ferric sulfate solutions and natural magnesium-nickel hydrosilicates and nickel hydroaluminosilicate minerals, a fact that is of great scientific and practical interest.

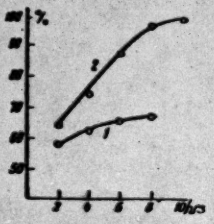

Fig. 4. Extraction of nickel from aidyrlite by leaching with ferric sulfate solutions: 1) 30 g/liter; 2) 45 g/liter.

Nickel can be almost completely leached by the investigated method of treatment with ferric sulfate solutions from the magnesium hydrosilicate minerals garnierite (Fig. 1), nepouite-garnierite (Fig. 2), and nickel cerolite and deweylite (Fig. 3). From its hydroaluminosilicate minerals aidyrlite (Fig. 4) and nickel aluminosilicate (Fig. 2), nickel can again be removed almost completely by leaching with ferric sulfate solutions.

These new experimental results on the interaction of various nickel-magnesium and nickel-aluminum hydrosilicate minerals with ferric sulfate solutions open up new prospects in the hydrometallurgy of nickel oxide-silicate ores. As previous investigations have shown [12], in these ores nickel is present mainly as nickel-magnesium and nickel-aluminum hydrosilicates of variable composition. In fact bunsenite is found very rarely and in very small amounts in nickel oxide-silicate ores. Since nickel-magnesium and nickel-aluminum hydrosilicates are leached out fairly readily with ferric sulfate solutions, it may be expected that nickel will be leached fairly readily from its oxide-silicate ores by the proposed leaching procedure with the aid of the solutions indicated.

Special investigations confirmed this practical conclusion. We showed experimentally that the proposed procedure of leaching with ferric sulfate solutions extracts up to 95.16% of the nickel in Ufalei oxide-silicate nickel ore, up to 96.71% of the nickel in Batashin oxide-silicate nickel ore, and, moreover, up to 95.71% of the nickel in the waste Aiderbak oxide-silicate ore.

Owing to the adequate efficiency of the method previously proposed by us for the leaching of oxide-silicate nickel ores with ferric sulfate solutions [2], there are great possibilities of lowering the consumption of sulfuric acid in the hydrometallurgical treatment of these ores. The sulfuric acid that is consumed in enormous amounts in reactions with iron and its compounds is not removed from the cycle of production, but is utilized in repeated leachings with sulfate solutions with the result that the expense of each treatment is reduced.

Apart from the advantage of utilizing sulfuric acid that has reacted with iron in the course of the leaching of iron-nickel oxide ores, there are great practical advantages in the method that we have developed [3] with respect to the possibility of preparing the sulfuric acid solutions required for hydrometallurgical treatments from waste sulfurous gases. Treatment of waste iron sulfate lyes with air and sulfurous gases [2, 3] provides the ferric sulfate solutions required, the sulfurous gases being utilized for the regeneration of sulfuric acid in solution.

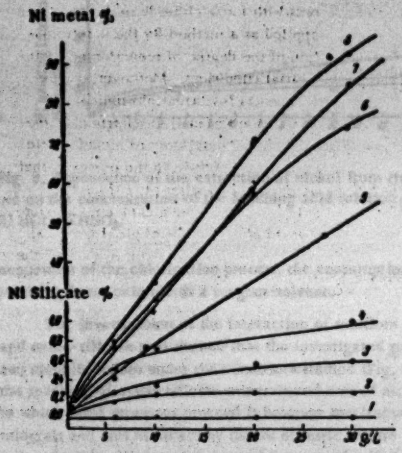

Fig. 5. Passage of nickel into solution in the course of leaching with ferric chloride solutions: 1) garnierite for 1, 2, and 3 hours at 15°; 2) garnierite for 0.5 hour at 100°; 3) metallic nickel for 1 hour at 15°; 4) garnierite for 2 hours at 100°; 5) metallic nickel for 1 hour at 15°; 6) metallic nickel for 2 hours at 15°; 7) metallic nickel for 0.5 hour at 100°; 8) metallic nickel for 1 hour at 100°.

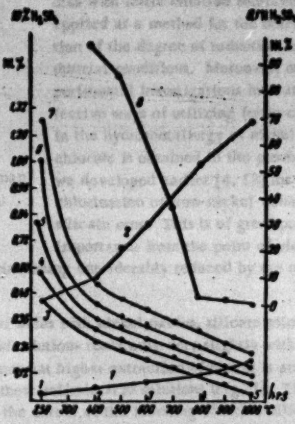

Fig. 6. Reaction of nickel oxides and their solid solutions with sulfuric acid solutions: 1) reaction of nickelous oxide with 10% H_2SO_4 solution at 10° for 1-5 hours; 2) reaction of nickelic oxide with 10% H_2SO_4 solution at 10° for 1-5 hours; 3) reaction of solid solutions of nickel oxides with 10% H_2SO_4 solution at 10° for 1 hour; 4) reaction of solid solutions of nickel oxides with 10% H_2SO_4 solution at 10° for 2 hours; 5) reaction of solid solutions of nickel oxides with 10% H_2SO_4 solution at 10° for 3 hours; 6) the same, for 4 hours; 7) the same, for 5 hours; 8) reaction of nickelous oxide with 0.1 N H_2SO_4 at 80° (the temperature (°C) at which the solid solutions of nickel oxides are prepared and the duration of the process (hours) are plotted along the axis of abscissae).

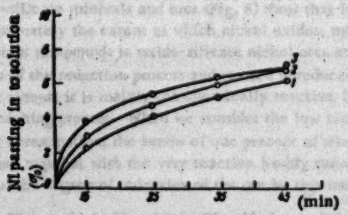

Fig. 7. Passage of nickel into solution during the leaching of nepouite-garnierite: 1) 1% H_2SO_4 solution; 2) 2% H_2SO_4 solution; 3) 3% H_2SO_4 solution.

It has thus been shown experimentally that the utilization of waste iron liquors in the manner proposed by us earlier [2,3] considerably reduces the total consumption of sulfuric acid, which can be obtained directly in the course of the leaching by the utilization of waste sulfurous gases, these being applied in the aeration of the pulp. Such a procedure is very economical.

The results of our experimental investigation of the interaction of ferric chloride solutions and mineral acids with nickel oxides and oxide-silicate nickel minerals and ores present not only technological, but also analytical interest. Under the conditions investigated (without warming the pulp or the use of high pressures) ferric chloride solutions do not react appreciably with nickelous oxide and garnierite, and they react only slightly with these during the boiling of the pulp. On the other hand, active metallic nickel obtained by reduction of nickelous oxide with hydrogen dissolves almost completely during leaching under the investigated conditions with ferric chloride solutions containing 30 g/liter and more of iron (Fig. 5). This gives us reason to suppose

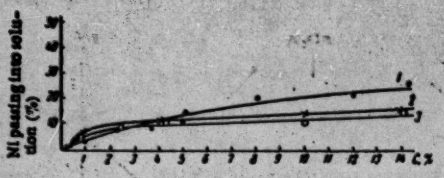

Fig. 8. Dependence of the extraction of nickel from rich Akkerman ore on the concentration of the leaching acid solution: 1) H_2SO_4; 2) HCl; 3) HNO_3.

that the leaching of reduced nickel oxides and oxide-silicate minerals and ores with ferric chloride solutions can be applied as a method for the determination of the degree of reduction under industrial conditions. Moreover, our experimental investigations indicate effective ways of utilizing ferric chloride in the hydrometallurgy of nickel: ferric chloride is obtained in the processes that we developed earlier [4, 13] for the chlorination of iron-nickel-cobalt oxide-silicate ores. This is of great practical importance from the point of view of the economics of the chlorination process, the consumption of chlorine being considerably reduced by the use of the resulting ferric chloride as a reagent-solvent.

The investigation of the interaction of solutions of mineral acids with nickel oxides, silicate minerals, and oxide-silicate ores showed that the investigated sulfuric acid solutions react only very slightly with nickelous and nickelic oxides under the conditions studied (Fig. 6). A somewhat higher extraction of nickel is attained in the leaching of oxide-silicate minerals and ores of nickel with these sulfuric acid solutions (Fig. 7). The extent to which these processes proceed is however much smaller than the extent of the leaching of oxide-silicate minerals and ores of nickel by means of ferric sulfate solutions. Our experiments show that the leaching of unreduced oxide-silicate nickel ores by means of sulfuric acid solutions is not sufficiently effective, a fact that can be explained completely by the physicochemical characteristics of these ores, which have been studied previously [12].

Experiments on the leaching of nickel oxides and silicate nickel minerals with nitric acid solutions showed that this process proceeds even more slowly than in the case of leaching with sulfuric acid solutions. For example, when nickelous oxide is leached with 20% nitric acid solution for two hours, only traces of nickel pass into solution, and in the leaching of nepouite-garnierite under the same conditions only about 1% of the nickel present is removed, i.e. only oxidized nonsiliceous nickel compounds – which are present in various amounts in oxide-silicate nickel minerals – pass into solution.

Our experimental results on the interaction of solutions of sulfuric and nitric acids with nickel oxides and oxide-silicate minerals and ores (Fig. 8) show that it is possible to use treatments with these acids to determine approximately the extent to which nickel oxides, minerals, and ores have been reduced by hydrogen. Since the nickelous sompounds in oxide-silicate nickel ores are reduced almost completely [10, 14] in the very earliest stages of the reduction process and roasted unreduced nickel silicates react with these solutions only to a very slight extent, it is mainly the chemically reactive freshly reduced metallic nickel that passes into solution in the leaching process. When we consider the low nickel contents of the low-grade and waste iron-nickel ores under investigation, the tenths of one percent of silicate nickel in the unreduced residues which may pass into solution together with the very reactive freshly reduced nickel will represent a negligible error in the determination of the degree of reduction of the ore by this method.

The method of leaching with sulfuric or nitric acid is much less applicable to the determination of the extent of reduction of oxide-silicate nickel ores with carbon monoxide (or gases containing carbon monoxide) or with solid carbon. As our previous investigations have shown [15, 18], nickel reduced under these conditions is of low reactivity in hydrometallurgical processes and so passes into solution much more slowly and less completely during leaching. The fact, which we established for the first time [2, 15], that there is a substantial fall in the solubility of nickel as the temperature at which it is reduced is raised makes this method completely inapplicable in this case.

Before the present investigations there was no exact method for the determination of the extent of reduction of nickel and cobalt oxides, minerals, and ores, and it may be considered that the approximate method that we have proposed for this purpose will have some importance for control and analysis.

There are no references in the literature to the possibility of effective selective leaching of nickel from its silicates with ferric sulfate solutions. The statement of Herrenschmidt [11] that ferric sulfate solutions react actively with nickelous oxide was not confirmed in our investigations.

Special experiments showed that nickelous oxide reacts to a negligible extent with ferric sulfate solutions, even under optimum conditions which result in almost complete extraction of nickel from its oxide-silicate minerals and ores.

In conclusion, the authors thank G. S. Gritsaenko, L. G. Berg, S. P. Gandelman, and the director of the Nickel-Cobalt Board of the Ministry of Nonferrous Metallurgy of the USSR, A. A. Mironov, for active participation and cooperation in the work.

SUMMARY

1. Metallic nickel freshly formed by reduction with hydrogen is almost completely dissolved during interaction with solutions of ferric chloride and mineral acids under the conditions investigated. Hence, before being leached with these solvents, iron-nickel oxide and oxide-silicate ores must be subjected to reduction with hydrogen or with technical or natural gases enriched as far as possible in hydrogen.

2. Ferric sulfate solutions of the compositions investigated interact considerably more intensively with nickel-magnesium and nickel-aluminum hydrosilicate minerals than solutions of ferric chloride and mineral acids; under suitable conditions they leach nickel from these minerals with an adequate degree of efficiency.

3. Nickel can be extracted almost completely from its various oxide-silicate minerals and ores by the proposed method of leaching with ferric sulfate solutions.

4. It was shown experimentally that it is possible to attain a high extraction of nickel from waste and low-grade iron-nickel oxide-silicate ores from various commercially worked deposits by the method of leaching with ferric sulfate solutions, which are readily obtained from recirculated iron-containing sulfate lyes by very simple methods.

5. It was shown that our previously proposed method [2] of making simultaneous use of recirculated iron-containing sulfate lyes and waste sulfurous gases for the preparation of the necessary sulfuric acid solutions substantially reduces the total consumption of acid in the sulfuric acid method of leaching oxide and oxide-silicate iron-nickel-cobalt ores.

6. It was shown that the methods investigated are of importance for control and analysis.

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SURFACE AND SORPTION PROPERTIES OF ACTIVE CARBONS

COMMUNICATION 2. INVESTIGATION OF THE EFFECT OF CHEMICALLY ADSORBED AND CHEMISORBED OXYGEN ON THE ADSORPTION PROPERTIES OF ACTIVE CARBONS WITH RESPECT TO WATER VAPOR

M. M. Dubinin and E. D. Zaverina

A review of the literature and a generalization of the results of previous investigations were given in a paper by one of the authors [1]. According to the experimental conditions, for active carbons previously evacuated at 1000° interaction with oxygen through chemical forces constitutes either chemical adsorption (up to about 100°) or chemisorption, which is marked at temperatures of about 200° and higher. These processes result in the formation of surface carbon oxides, the functional properties of which depend on the temperature at which the sorption of oxygen occurs.

The effect of surface oxides formed by reaction between active carbons and oxygen at 350-500° on the adsorption of various vapors has been studied by Bruns and Maksimova [2] and by us [3-6]. The elementary compositions of carbons containing surface oxides were studied in one of our investigations [7]. Hence, the effect on the adsorption of various vapors of the presence of acidic surface oxides formed at relatively high temperatures (350-500°) has been subjected to fairly detailed investigation. We are not aware of any investigation on the effect of chemically adsorbed and chemisorbed oxygen in the initial chemisorption range, i.e. 200°, on the adsorption of vapors. Investigation in this direction formed the main purpose of the present work.

EXPERIMENTAL

1. In order to exclude as far as possilbe the part played by chemically adsorbed oxygen, it was necessary to carry out the thermal treatment of the weighed sample of carbon in a vacuum at 1000° and then, after cooling with continued evacuation to the experimental temperature of 20°, measure the adsorption isotherm of vapor without bringing the carbon into contact with atmospheric oxygen. In accordance with the aims of the investigation, the previously evacuated carbon must then be brought into contact with oxygen under the conditions for chemical adsorption or chemisorption. The apparatus must therefore provide for the direct determination of the amount of chemically bound oxygen from the increase in weight of the carbon and for the subsequent measurement of the adsorption isotherm for vapor.

For the performance of these tasks we used the sorption-balance method. The previously described apparatus for the measurement of sorption isotherms [8] was modified, the design of the tube and sorption balance being altered. The new sorption tube was constructed of thick-wall quartz in its lower part (560 mm) and it had a diameter of 40 mm and total length of 920 mm. The upper part of the tube (360 mm) was made of glass and was attached to the lower part by means of a ground joint. The lower end of the tube was closed, and the upper end carried a ground-in stopper provided with a hook for the attachment of the sorption balance.

The stopper was mercury-sealed, and a side tube on the glass part of the tube connected it through a mercury seal to the unchanged part of the apparatus, which included a U-shaped mercury manometer, a McLeod gage, and a funnel with a porous base for the introduction of gas (oxygen, hydrogen, vapor of liquid to be adsorbed) into the system through a layer of mercury.

A quartz spiral was hung on the hook in the stopper; it had a sensitivity of 0.0145 mg for each division of the ocular screw micrometer of the cathetometer, which corresponded to 0.0025 mm. There was a hook at the

lower end of the quartz spiral, and this carried a quartz thread, weight 100 mg and length 895 mm, and a thin-walled quartz sphere, diameter 10 mm, which was provided with a hook and two side openings. The carbon (about 100 mg) was placed in the sphere, which weighed 46.3 mg. The sphere was at about 75 mm from the sealed end of the quartz tube. The use of spherical vessel having two side openings in its upper part (diameter about 2mm) instead of an open dish, largely prevented the scattering of carbon in the initial stage of evacuation.

With the aid of a wide clamp placed near the joint, the sorption tube was fixed in a strictly vertical position to a massive metal stand in such a way that there was free access to the lower end of the tube. A simple lifting device made it possible to place the lower part of the sorption tube into an electric tube furnace with a platinum winding or into an ultrathermostat. The furnace tube was 65 mm in diameter and 300 mm in length. The body of the furnace was furnished with a water-cooled copper jacket to prevent any heating of the apparatus by rising currents of hot air. The lower opening of the furnace tube was closed by sheets of asbestos paper. When the furnace was in position, complete closure at the upper opening was effected with the aid of asbestos gaskets which fitted around the sorption tube. In this working position, the sphere containing the carbon was in a constant-temperature zone. The temperature was measured with a thermocouple of platinum and platinum-rhodium, which was placed in the space between the furnace tube and the quartz tube at the level of the sphere containing the sample of carbon.

2. The materials investigated were two ashless active carbons prepared by the activation of the carbonization product from sucrose by means of carbon dioxide at 850°. For Carbon 1 the combustion loss due to activation was 6%, and for Carbon 2 it was about 20%. Both carbons belonged to the first structural type [9]. The constants for the adsorption-isotherm equation for the standard vapor (benzene) were:

Carbon 1: $W_0 = 0.093$ cc/g; $B = 0.552 \cdot 10^{-6}$
Carbon 2: $W_0 = 0.305$ cc/g; $B = 0.547 \cdot 10^{-6}$

The equation of the adsorption isotherm for active carbons of the first structural type was found to be closely obeyed over a wide range of relative pressure (from $1 \cdot 10^{-5}$ to 0.4). It will be seen that the selected carbons differed greatly in limiting sorptive capacity, whereas the constant B, which characterizes the curvature of the isotherm in the initial region, is almost the same for both carbons. In the course of the investigation it was found to be desirable to use Carbon 1 in the form of a rather coarse fraction that did not contain carbon dust. The screened fraction having grains that pass 0.5 mm mesh but not 0.25 mm mesh will be referred to as Carbon 1k. With respect to adsorption properties, Carbons 1 and 1k were almost identical.

Owing to the relatively low volume of micropores in Carbon 1, this carbon had distinct advantages in investigations on the cause of the relatively low values of sorption in the region of the filling of the micropores. With respect to the volume of micropores, Carbon 2 differed little from technical carbons.

Water vapor was used as adsorbate, for it is most sensitive to changes in the chemical state of the carbon surface due to changes in the number of primary adsorption centers [5]. A great reduction in the number of primary adsorption centers was brought about by thermal treatment of the active carbon in a vacuum at 1000°. The experiments of this series, which is denoted by the letter A, were carried out under the following conditions: 4 hours at 1000° under evacuation by a three-stage mercury pump. Pumping was continued while the carbon was cooled to 20°. The system was then disconnected from the evacuation apparatus by a turn of a tap, the loss in weight of the carbon sample was determined, and the sorption isotherm for water vapor was measured without allowing the carbon to come into contact with atmospheric oxygen (such contact occurred in experiments of previous investigators).

In experiments of Series B, the carbon evacuated and cooled to 20° under the above-described conditions was brought into contact with oxygen at a pressure of 50 mm. The oxygen was prepared by the thermal decomposition of chemically pure potassium permanganate. When the carbon had been kept in the oxygen atmosphere for 12-14 hours, the vessel was evacuated until the carbon sample attained a constant weight. The increase in weight of the carbon due to irreversible chemical adsorption of oxygen was measured. Sorption isotherms for water vapor were then measured.

In order to study the effect of the presence of chemisorbed oxygen on adsorption, the carbon, after evacuation at 1000° (or at 450° in certain experiments), was cooled to 200° and oxygen was admitted up to a pressure of 50 mm. The carbon was kept in contact with oxygen at 200° for ten hours. After the carbon had been cooled

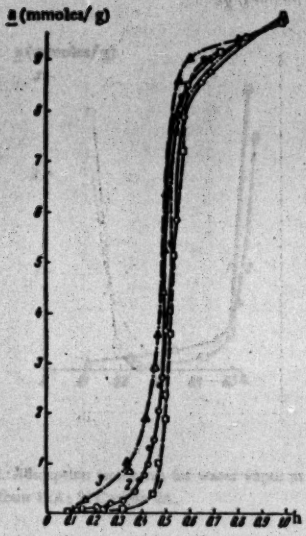

Fig. 1. Sorption and desorption isotherms for water vapor at 20°: 1) Carbon 1A; 2) Carbon 1; 3) Carbon 1C (the black points correspond to the desorption branches).

to 20°, the apparatus was evacuated at this temperature until the carbon attained constant weight. The sorption isotherm for water vapor was then measured. These experiments comprised Series C.

In order to estimate the effect of a reducing atmosphere on the destruction of surface carbon oxides, in some experiments the thermal treatment of the carbon was carried out in an atmosphere of hydrogen at 1000° (Series D). For this purpose the carbon was first evacuated for six hours at 450°, cooled to 20°, and weighed (initial weight). The temperature was raised, and when it attained 450° hydrogen was admitted into the system up to a pressure of about 100 mm. Heating was continued to 1000°, and the carbon was kept at this temperature for four hours. On the next day the carbon was again heated to 1000° for one hour, after which the mercury pump was turned on and the carbon was evacuated for one hour. After cooling to 20° under evacuation, the carbon was weighed and the adsorption isotherm was determined for water.

As these preliminary treatments of the carbons affected the chemical properties of their surfaces, the samples obtained were described by the Carbon number and the Series letter, for example Carbon 2A. For each variant of preliminary treatment, several experiments were generally carried out. Where essential, therefore, apart from these characterizations of the carbon, the number of the experiment will be given. In most cases conclusions were drawn on the basis of the mean results of experiments.

Apart from the above measurements, we made the usual measurements of sorption isotherms for water vapor on carbon samples that had been kept in sealed tubes in contact with air. In these cases, the preliminary evacuation of the carbons was carried out at 450° for six hours, after which the isotherms were determined. The carbons from these experiments will be denoted by a number only, e.g. Carbon 2.

3. For a general appraisal of the effect of the chemical state of the carbon surface on the form of the sorption and desorption isotherms for water vapor, preliminary experiments were carried out with Carbon 1 thermally treated in a vacuum at 1000° (Carbon 1A), the same sample of carbon with the usual state of the surface (Carbon 1), and a sample of carbon containing chemisorbed oxygen in the form of surface oxides (Carbon 1C). The results of the measurements on the sorption and desorption isotherms for water vapor at 20° are shown graphically in Fig. 1.

The isotherms indicate a very considerable effect of the chemical state of the carbon surface in the adsorption region. Carbon 1A, which has a preliminary evacuation at 1000°, adsorbs only small amounts of water vapor up to a relative pressure of h = 0.4 (Curve 1). At higher relative pressures there is a sharp rise in the adsorption branch of the isotherm. Carbon 1, which has the usual surface state and is kept in contact with atmospheric oxygen, contains chemically adsorbed oxygen on its surface in the form of surface oxides having a basic character. The presence of a larger number of adsorption centers results in increased adsorption in the initial region of the isotherm; the isotherm passes on to the sharp rise more smoothly and at lower relative pressures (Curve 2). Finally, in the case of Carbon 1C, the formation of considerable amounts of surface oxides as a result of chemisorption of oxygen at 200° leads to a considerable rise in the extent of adsorption in the initial part of the isotherm. The region in which the sharp rise occurs is still further displaced in the direction of lower relative pressures (Curve 3).

At high relative pressures the sorption and desorption branches of the isotherm do not coincide and form hysteresis loops which are characteristic of the sorption isotherms for water vapor on active carbons. Owing to

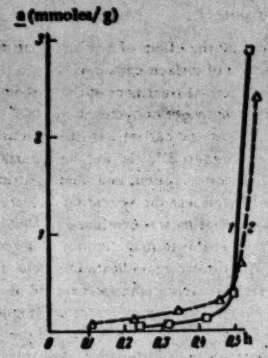

Fig. 2. Adsorption isotherms for water vapor at 20°: 1) Carbon 1kA; 2) Carbon 2A.

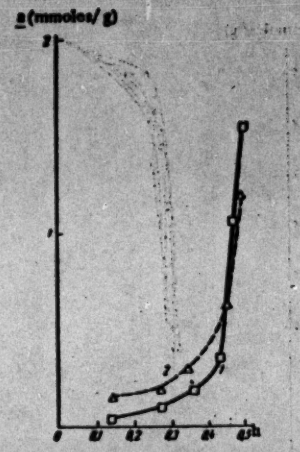

Fig. 3. Adsorption isotherms for water vapor at 20°: 1) Carbon 1kB; 2) Carbon 2B.

Fig. 4. Adsorption isotherms for water vapor at 20°: 1) Carbon 1C (○– Experiment 6; □– Experiment 7) and Carbon 1kC (◇ Experiment 20); 2) Carbon 2C (△ – Experiment 20; × – Experiment 15).

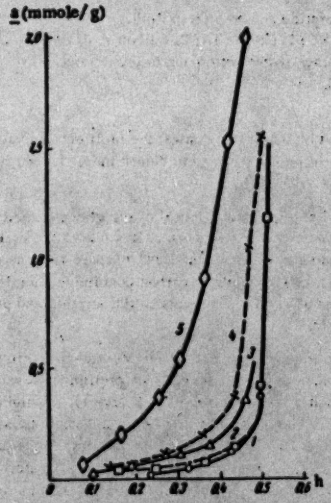

Fig. 5. Adsorption isotherms for water vapor at 20: 1) Carbon 1kA, Experiment 17; 2) Carbon 1kA, Experiment 18; 3) Carbon 1kB, Experiment 19; 4) Carbon 1kB, Experiment 19a; 5) Carbon 1kC, Experiment 20.

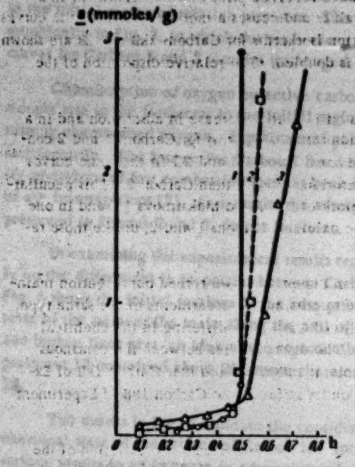

Fig. 6. Adsorption isotherms for water vapor at 20°: 1) Carbon 1kA, Experiment 17; 2) Carbon 1kD, Experiment 21; 3) Carbon 1kD, Experiment 22.

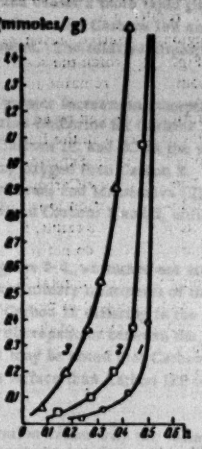

Fig. 7. Adsorption isotherms for water vapor at 20°: 1) Carbon 1kA, Experiment 17; 2) Carbon 1kB, Experiment 19a; 3) Carbon 1kC, Experiment 20.

the low combustion loss in the activation of Carbon 1 and its extremely fine state of porosity (for this carbon a reverse series is found for the adsorption of acetic, propionic, valeric, and heptanoic acids from aqueous solutions), the points for the start of hysteresis correspond to sorption values of 4-5 mmoles/g. At lower sorption values the sorption and desorption points fit satisfactorily on a single curve for each carbon sample, a fact that indicates the reversible character of the primary adsorption process.

In the hysteresis region, the effect of the chemical state of the carbon surface is not so marked and is due mainly to the displacement of the regions of sharp rise of the isotherms in the primary adsorption process. The limiting sorption values for Carbons 1A, 1, and 1C are almost the same and are found in the range 9.78-9.83 mmoles/g. The mean limiting sorption value for water vapor corresponds to a limiting sorption capacity of $v_s = 0.176$ cc/g. According to experiments with benzene, $v_s = 0.101$ cc/g, which is substantially less and is close to the value of the limiting adsorption capacity of this carbon $W_0 = 0.093$ cc/g. It follows from the results that Carbon 1 has an extremely fine microporosity, part of it being inaccessible to the larger molecules of benzene. For Carbon 1 we observe the typical effect of ultraporosity in the adsorption of vapors of substances having molecules of different sizes.

The main effect of the chemical nature of the surface of active carbon is therefore manifested in the adsorption region of the isotherm, which for Carbon 1 includes adsorption values up to 40-50% of the limiting values. This peculiar feature of Carbon 1 formed the basis of its choice as the main object for investigation.

It follows from these preliminary experimental results that it is desirable to concentrate attention on the study of the adsorption regions of isotherms for carbon samples having surfaces differing in chemical nature. The systematic investigation consisted in prior treatments of carbon samples by the above described procedures A, B, C, and D and the measurement of isotherms in the adsorption region.

In Fig. 2 a comparison is made between the initial sections of the adsorption isotherms for water vapor on Carbons 1kA and 2A, which have partially destroyed surface oxides as a result of the preliminary evacuation at 1000°. In accord with the higher specific surface of Carbon 2, at relative pressures of less than 0.5, its isotherm is in the higher position. However, as in Fig. 1, the region of sharp rise in the isotherm for this carbon is displaced in the direction of higher relative pressures. The reduction in the amount of surface oxides has led to a considerable reduction in the adsorptive power of the carbons with respect to water vapor at relative pressures up to 0.5.

Chemical adsorption of oxygen at 20° on active carbons that have received prior thermal treatment in a vacuum at 1000° results in a substantial increase in the adsorption values and causes a more rapid rise of the curves in the initial region of relative pressures. The experimental adsorption isotherms for Carbons 1kB and 2B are shown graphically in Fig. 3, in which the scale along the axis of ordinates is doubled. The relative disposition of the curves for Carbons 1 and 2 remains unchanged.

Chemisorption of oxygen by active carbons at 200° results in a still greater increase in adsorption and in a steeper rise in the isotherms in the initial region. Fig. 4 shows the adsorption isotherms for Carbons 1 and 2 containing chemisorbed oxygen. Experimental points for various samples of Carbons 1C and 2C fit the same curves satisfactorily. The less active Carbon 1 has a higher power of chemisorbing oxygen than Carbon 2. This peculiarity of carbons of low combustion loss has been noted already in the work of Bruns and Maksimova [2] and in one of our investigations [7]. As a result, the adsorption isotherms for the oxidized Carbons 1 and 2, unlike those represented in Figures 2 and 3, do not intersect.

In examining the experimental results represented graphically in Figures 2-4, we turned our attention mainly on the differences in properties between Carbons 1 and 2 subjected to preliminary treatments of the same type. Fig. 5 shows the initial sections of the adsorption isotherms for samples of Carbon 1k differing in the chemical state of the surface; the scale along the axis of ordinates is doubled. The discrepancies between the continous and broken lines give an idea of the reproducibility of the experiments; it may be noted that Carbon 1kB of Experiment 19 contained about 20% more chemically adsorbed oxygen on its surface than Carbon 1kB of Experiment 19.

The curves in Fig. 5 indicate the considerable variation of the adsorption values with the variation of the chemical state of the surface of Carbon 1k. Increase in the content of oxygen chemically bound at the carbon surface results in an increase in adsorption values in the initial sections of the isotherms and in a displacement of the regions of sharp rise toward lower relative pressures.

Thermal treatment of Carbon 1k in hydrogen at 1000° (the preliminary evacuation of the carbon for the determination of its original weight was also carried out at 1000°) resulted in an appreciable ignition loss: 1.37% in Experiment 21 and 1.89% in Experiment 22. These Series D active carbons were evacuated to remove hydrogen at 1000° and cooled under constant pumping to 20°; adsorption isotherms for water vapor were then determined without bringing the carbons into contact with atmospheric oxygen. In Fig. 6 a comparison is made between the isotherms so obtained and the adsorption isotherm for Carbon 1kA, which received only thermal treatment in a vacuum at 1000°. The effect of the treatment of the carbons in hydrogen is shown by appreciably increased adsorption in the initial region of the isotherm and a somewhat less abrupt rise to the steep almost linear section of the curve (h = 0.5-0.7), as compared with Carbon 1kA. These effects are enhanced in the sample carbon having the higher ignition loss in the hydrogen atmosphere. Hence, thermal treatment of a carbon at high temperature in a hydrogen atmosphere also results in chemical modification of the surface of the active carbon.

4. Theoretical concepts relating to the mechanism of the adsorption of water vapor [10-13] made it possible to derive an equation for the adsorption isotherm for the region of unimolecular coverage of the carbon surface [5]. To the first approximation, this equation expresses the most characteristic features of the adsorption of water vapor by carbon adsorbents; it has the form:

$$a = \frac{a_0 ch}{1 - ch}, \qquad (1)$$

in which a_0 is the number of primary adsorption centers on the carbon surface, c – is the ratio of kinetic constants, and $h = p/p_s$ is the relative pressure. Equation 1 is applicable for relative pressures of less than 1/c. As c and h are dimensionless quantities, the number of primary adsorption centers a_0 is expressed in the same units as the adsorption a.

The values of the constants a_0 and c can be readily determined from the parameters of the straight line corresponding to the isotherm equation (1) in the linear form:

$$\frac{h}{a} = \frac{1}{a_0 c} - \frac{1}{a_0} h: \qquad (2)$$

The table gives the constants a_0 and c of Equation 1 for various samples of active carbon, including some studied in the preceding investigation [6].

TABLE

Constants in the Equation for the Adsorption Isotherm

Carbon	Experiment	a_0 (mmole/g)	c
1kA	17	0.033	1.85
1kA	18	0.037	1.85
1kB	19	0.090	1.78
1kB	19a	0.091	1.93
1kC	20	0.437	1.83
2A	9	0.007	1.72
2B	10	0.169	1.82
2C	14	0.280	1.84
2C	15	0.274	1.90
E-1	Dubinin and Zaverina[6]	1.35	1.87
E-2	[6]	1.43	1.85
E-3	"	0.110	1.69
E-4	"	0.205	1.50
B	Bruns [2]		1.71
C	"	0.075	1.58

According to the table, the number of primary adsorption centers in Carbon 1kB, which contains chemically adsorbed oxygen, is 2.5 times as great as in Carbon 1kA, which was ignited in a vacuum at 1000°. Oxidation of the carbon with oxygen at 200° (Sample 1kC) results in an increase in the number of primary adsorption centers, which is 12.5 times as great as in Carbon 1kA. Carbon 2B has 1.8 times as many primary adsorption centers as Carbon 2A. Oxidation of Carbon 2 at 200° (Carbon 2C) is accompanied by an increase in the number of primary adsorption centers by a factor of only 2.9, as compared with Carbon 2A. As compared with Carbon 1, Carbon 2 has a greater number of primary adsorption centers after evacuation at 1000° and after chemical adsorption of oxygen at 20°, but, as already noted, in oxidation with oxygen at 100° Carbon 2 acquires fewer primary adsorption centers than Carbon 1.

Chemisorption of oxygen at 450° results in a still greater increase in the number of primary adsorption centers, which attains 1.5-3 mmoles/g (Carbons E-1, E-2, and B; see Table); this number falls sharply after themal treatment of the oxidized carbons in a vacuum at 900-1000° (Carbons E-3, E-4, and C; see Table).

The extent to which the experimental results correspond to the adsorption isotherm (1) can be judged from Fig. 7, in which the adsorption isotherms calculated from the values of a_0 and $\underline{c}$ given in the table are represented by continuous lines and the experimental points are represented in various ways.

5. Carbon 1k evacuated at 1000° and brought into contact with oxygen at 20° and about 50 mm for 12-14 hou hours adsorbed oxygen to the extent of $a^0 = 0.110$ mmole/g (Experiment 19) or $a^0 = 0.115$ mmole/g (Experiment 19a). The value of the adsorption a^0 expresses the sum of the amounts of physically and chemically adsorbed oxygen. Exposure to a high vacuum at 20° to constant weight of carbon (two hours) results in the removal of physically adsorbed oxygen. The residual adsorption represents irreversible chemical adsorption of oxygen, $a = 0.064$ mmole/g (Experiment 19) and $a = 0.074$ mmole/g (Experiment 19a). For an unscreened sample of the carbon we obtained $a = 0.099$ mmole/g (Experiment 4). In the case of Carbon 2 under similar conditions we obtained $a = 0.121$ mmole/g (Experiment 10) and $a = 0.095$ mmole/g (Experiment 13). Hence, on the average the values of the chemical adsorption of oxygen at 20° were $a = 0.069$ mmole/g for Carbon 1k and $a = 0.108$ mmole/g for Carbon 2.

Chemisorption of oxygen by carbon at 200° is accompanied by appreciable formation of carbon dioxide, which can be detected in the equilibrium gas phase [1]. Hence, the change in weight of the carbon is the net result of an increase due to chemisorption and a decrease due to ignition loss of the carbon. Thus, in Experiment 7 on Carbon 1 there was no appreciable change in the weight of the carbon, in Experiment 20 Carbon 1k there was a diminution of 0.30% in the weight of the carbon, and in Experiment 14 on Carbon 2 there was an increase in weight of 0.41%. Hence, the amount of chemisorbed oxygen cannot be judged by the change in weight of the carbon resulting from oxidation.

DISCUSSION OF RESULTS

The question of the nature of the primary adsorption centers on the surface of carbon adsorbents — in particular, active carbons — is of fundamental importance for the discussion of our results. The results of the present investigation show that the adsorptive power of active carbons for water vapor in the region of unimolecular coverage is greatly dependent on the amount of oxygen chemically bound to the carbon surface. This is shown in the close relationship between the constant a_0 of Equation 1 for the adsorption isotherm, i.e. the number of primary adsorption centers in millimoles per gram, and the amount of chemically adsorbed or chemisorbed oxygen.

For several technical reasons we were unable to treat the investigated samples of active carbon at temperatures above 1000°. For such carbon samples of Series A (Carbons 1kA and 2A), although the number of primary

adsorption centers was greatly reduced (e.g. to 0.33 mmole/g for Carbon 1kA), it did not become zero. Thermal treatments at higher temperatures have been used for nonporous carbon adsorbents, namely carbon black. Raising of the temperature of the treatment of carbon black over the range 1000-2800° yields samples for which the regions of the isotherm associated with the sharp rise are displaced toward higher relative pressures. The curves representing the isotherms become less and less steep, and the adsorption values for unit surface of the carbon black diminish [12, 14]. For carbon black ignited in a vacuum at about 2800°, the adsorption of water vapor remains negligibly small up to h = 0.95 [14].

There can be no doubt that thermal treatment of carbon adsorbents in the temperature range 1000-2800° results in further reduction in the number of primary adsorption centers. However, the causes of this reduction may vary in character. In the first place, it may be a question of further destruction of particularly stable surface oxides. In the investigations cited, however, the experimental procedure differed from ours: after thermal treatment at high temperature the carbon black was cooled to room temperature and brought into contact with atmospheric oxygen for weighting and transference to the sorption apparatus. As our experiments show, under such conditions chemical adsorption of oxygen occurs on particularly active sites containing carbon atoms with unsaturated valencies, so that there is re-formation of surface oxides that act as primary adsorption centers.

Thermally treated carbon black in contact with atmospheric O_2 shows no appreciable tendency to acquire primary adsorption centers comparable to the original numbers. Such carbon black loses power to form an appreciable number of primary adsorption centers on its surface. This may result from recrystallization of carbon with formation of considerably larger crystals. Hence, the number of active sites (having unsaturated valencies, e.g. fragments of carbon side chains consisting of 1-2 atoms [1]) per unit surface area of the carbon is greatly reduced and the extent of chemical adsorption is similarly reduced. Consequently, the growth in carbon crystallites accompanying the reduction in the energetic heterogeneity of the surface is probably the main cause of the reduction in the number of primary adsorption centers resulting from thermal treatment of carbon black above 1000° (which, according to x-ray data, is the temperature at which appreciable growth of crystallities begins). It is thus found that, by the oxidation of Graphon carbon (prepared from carbon black by thermal treatment at 2800°), it is impossible to prepare adsorbents in which the number of primary adsorption centers is at all comparable to the number in the original carbon black, ignited at more moderate temperatures (up to 1000°).

Hence, the question of the nature of the majority of the primary adsorption centers in carbon adsorbents ignited in a vacuum at 1000° remains an open one. It is doubtful whether all of them can be associated with chemically adsorbed oxygen atoms. On the other hand, it is very unlikely that they can be associated with the ash elements present in the carbons, for a reduction of almost a hundred-fold in the ash of the carbons (treatment with hydrofluoric and hydrochloric acids and subsequent washing) does not effect the form of the adsorption isotherms for water vapor to an appreciable extent [6, 15]. The carbons were prepared from twice-recrystallized sucrose contained less than 0.005% of ash. If we assume that all the ash in such carbon consists of SiO_2, then 1 g of carbon will contain $8 \cdot 10^{-4}$ mmole/g SiO_2. Not all of the SiO_2 molecules can be hydrated with formation of OH groups that can act as primary adsorption centers. Such a process can result in the formation of only a few OH groups on the surface of the ignited silicon dioxide. In all, the number of possible primary centers due to ash elements will be less than that observed for carbons of Series A by a factor of 10-100. It may be added that the ash of technical carbons activated with gaseous substances (the product of the complete ashing of the carbons) adsorbs only an extremely small amount of water vapor [15].

Laying aside the question of the nature of the primary adsorption centers in carbons ignited in a vacuum at 1000°, we may consider the question of the additional, very substantial number of adsorption centers formed as a result of the chemical adsorption of oxygen at 20°. According to the table, as we pass from Carbon 1kA to Carbon 1kB, the number of primary adsorption centers increases by:

$$0.090 - 0.035 = 0.055 \text{ mmole/g}$$

This increase is due to the chemical adsorption of oxygen, which amounts to 0.069 mmole/g on the average. Hence, as a result of the chemical adsorption of one molecule of oxygen, approximately one primary adsorption of one molecule of oxygen, approximately one primary adsorption center is formed. An analogous estimate for the passage from Carbon 2A to Carbon 2B gives a change in the number of primary adsorption centers of

$$0.169 - 0.097 = 0.072 \text{ mmole/g}$$

as a result of chemical adsorption of oxygen to the extent of 0.108 mmole/g. We again obtain the same relationship, although the approximation is not so close.

It is important to note that the values we have found for the chemical adsorption of oxygen— from 0.069 mmole/g for Carbon 1 to 0.108 mmole/g for Carbon 2— lie in the range 0.080-0.150 mmole/g, as found by various methods for various active carbons [1].

As already pointed out, the interaction of oxygen with active carbons at 200° is accompanied by appreciable ignition loss. Loebenstein and Deitz have recently made a detailed study of the chemisorption of oxygen by various carbons at 200° by careful analysis of the gas phase and desorption products [16]. These authors found that, in the interaction of active carbon prepared from coconut shell with oxygen at 200°, chemisorption of oxygen amounted to 0.47 mmole/g and, on the average, about 1.3 mmoles/g of oxygen was consumed in the oxidation of the carbon with formation of gaseous products, mainly carbon dioxide. It is therefore not surprising that in many experiments we observed a small loss in the weight of carbon after chemisorption of oxygen at 200°. It may be noted that the amount of chemisorbed oxygen in the experiments of Loebenstein and Deitz on coconut-shell carbon ($a = 0.47$ mmole/g) is close to the number of primary adsorption centers for Carbon 1kC after chemisorption of oxygen at 200° ($a_0 = 0.437$ mmole/g). It would appear that, under these conditions also, one primary adsorption center is formed as a result of the chemisorption of about one molecule of oxygen. This number may be high, but it is unlikely that it will be more than double the true value.

If we assume, as a first approximation, that in the case of Carbon 1kC with a number of primary adsorption centers of $a_0 = 0.437$ mmole/g every center is formed as a result of the chemisorption of one molecule of oxygen, then, in conformity with chemisorption of oxygen to the extent of $a = 0.437$ mmole/g, the oxygen content of the carbon should be about 1.4%. This amount lies within the limits of possible oxygen content for an active carbon that has interacted with air at 200° for a longer time [7]. It will be important in the future to have direct data, based on chemical analysis, on the oxygen contents of such carbons.

It must be pointed out that the oxidation of an active carbon by oxygen at a still higher temperature, e.g. 450°, results in a further increase in the number of primary adsorption centers formed by the chemisorption of oxygen (see Table, Carbons E-1, E-2, and B).

The chemical changes in the surface of active carbons due to thermal treatment in a hydrogen atmosphere at 1000° have received little study. The appreciable ignition loss of the carbon is not surprising, for the interaction of active carbons with hydrogen at high temperatures with formation of methane has been referred to several times in the literature [17]. However, on the basis of the isotherms in Fig. 6 it may be concluded that the ignition of carbon in a hydrogen atmosphere results in an increase in the number of primary adsorption centers. It is possible that these arise as a result of the formation of surface compounds of hydrogen with carbon. Further investigations in this direction will be of undoubted interest.

SUMMARY

1. An experimental procedure was developed and was applied to the study of the effect of the chemical state of the surface of an active carbon— as determined by chemical adsorption or chemisorption of oxygen— on adsorption isotherms for water vapor.

2. It was shown that the formation of surface oxides has a very substantial effect, particularly on the adsorption region of the isotherm.

3. The question of the nature of the primary adsorption centers on the surface of active carbons was discussed on the basis of the experimental results. It was shown that the chemical adsorption of one molecule of oxygen results in the formation of approximately one primary adsorption center.

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EFFICIENCY OF PROTECTOR BLOCKS OF ALUMINUM – ZINC ALLOYS

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Akimov [1] and Tomashov [2] have shown that protector blocks of Al–Zn alloys have considerable advantages over those made of pure zinc or aluminum. In their investigations, however, the aluminum content of the zinc alloys was not more than 10%, and the zinc content of the aluminum alloys was also not more than 10%.

EXPERIMENTAL

In the present work, Al–Zn alloys in the central part of the system were investigated (Fig. 1). The compositions of the alloys are given in the table. The alloys were prepared from Grade 00 aluminum and Grade 0 zinc. The iron, silicon, and copper contents of all the alloys did not exceed the permissible limits for the original metals. The tests were carried out in 1.5% sodium chloride solution. The ratio of the area of the steel sample to the area of the protector block was 13 : 1. The relation between the protective current per unit area of protector block (measured ten days after the start of the tests) and the composition of the block is shown in Fig. 2, from which it follows that the highest protective current is given by Alloys 2, 3, and 4, which contain 30–70% of zinc.

TABLE

Chemical Compositions of the Alloys Investigated.

Alloy No.	Content (%) of	
	Al	Zn
1	91.30	8.51
2	70.52	29.31
3	47.13	52.76
4	29.26	70.42
5	14.58	85.20
6	4.37	95.52

An investigation of the stationary electrode potentials of the alloys showed (Fig. 3) that with increase in the zinc content from 0 to 30% the potential of the alloy is markedly displaced in the negative direction. Further increase in the zinc content up to 70% has almost no effect on the stationary potential of the alloy. Further change toward pure zinc results in a further small movement in the negative direction. When a couple is formed with the steel to be protected, the potential of the protector block is displaced in the positive direction (the block is anodically polarized). It follows from Fig. 4 that the least polarized blocks contain 50–70% zinc. These alloys, which have a fairly high negative potential (Fig. 3) and a low polarizability, give the highest protective current. It is important that the protective current should fall as little as possible with time. It will be seen from Fig. 5 that in the course of ten days the protective current of protector blocks containing 30–70% zinc falls to 60% of its initial value, whereas for pure zinc it falls to 40% of its initial value and there is a particularly great fall in the case of an aluminum protector block (to 20% of its initial value). Hence, from this point of view also, the central part of the Al–Zn system is more satisfactory than pure aluminum or zinc. Another important characteristic of a protector material is the number of amp-hours obtained in the dissolution of 1 g of the protector block. It follows from Fig. 6 that this number increases as the aluminum content of the alloy increases.

These results indicate that alloys of the central part of the Al–Zn system can be used for the preparation of protector blocks. These alloys have potentials close to that of zinc, but they polarize anodically to a lower extent, give a high protective current, are more stable over a period of time, and show a smaller loss of protector material in providing the same quantity of electricity.

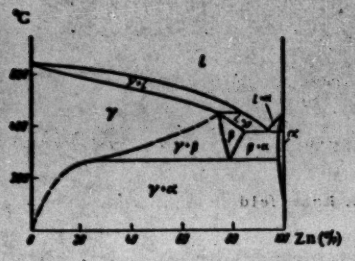

Fig. 1. Phase diagram of Al– Zn system.

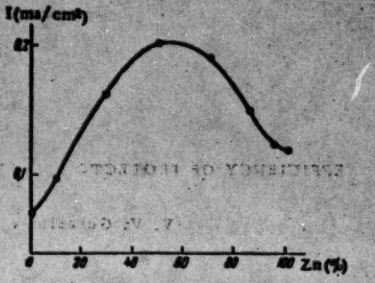

Fig. 2. Protective current per sq. cm of protector surface (ratio of area of protected surface to area of protector block = 13 : 1).

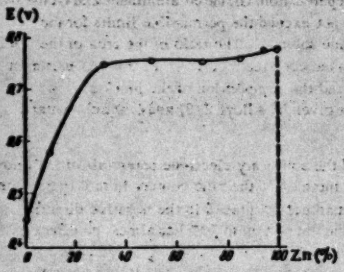

Fig. 3. Stationary electrode potentials of alloys of the Al– Zn system (with respect to the normal hydrogen electrode).

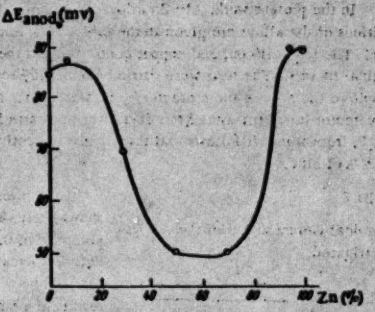

Fig. 4. Anodic polarizability of Al– Zn alloys for a current density of 1.5 ma/cm².

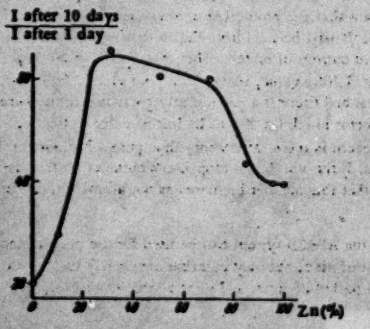

Fig. 5. Ratio of current given by protector after ten days to initial current (%).

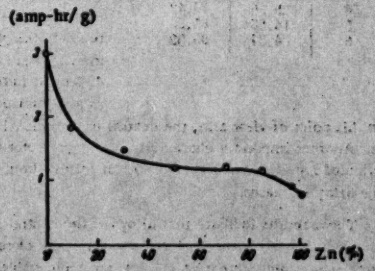

Fig. 6. Number of amp-hours obtained in the dissolution of 1 g of protector block.

Laboratory worker N. N. Ponsova took part in the experimental part of the work.

SUMMARY

1. An investigation was made of the stationary electrode potentials, the protective currents, the anodic polarizabilities, and the stability in use of six aluminum-zinc alloys together with pure aluminum and zinc.

2. It was shown that protector blocks of alloys containing 30-70% of zinc are more efficient than protector blocks made of pure aluminum or zinc or alloys of zinc content 0-30% and 70-100%.

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SYNTHESIS OF ALKENYL 2-CHLOROVINYL KETONES

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The great potentialities of the use of 2-chlorovinyl ketones in organic synthesis [1] prompt investigation into the possibility of preparing new types of compounds of this class. Methods of synthesizing alkyl 2-chlorovinyl ketones [2] and aryl 2-chlorovinyl ketones [3] are now well established. The present paper is devoted to the synthesis of alkenyl 2-chlorovinyl ketones of the type $R_2C{=}CHCOCH{=}CHCl$. The combination of very active 2-chlorovinyl and alkenyl groups conjugated with a carbonyl group in one molecule provides a basis for attempts to use these compounds in various syntheses.

We examined two possible ways of synthesizing alkenyl 2-chlorovinyl ketones. The first way, which is analogous to the method used for alkyl and aryl 2-chlorovinyl ketones, consisted in the direct condensation of acid chlorides of α,β-unsaturated acids with acetylene in presence of aluminum chloride:

$$R_2C{=}CHCOCl + CH{\equiv}CH \xrightarrow{AlCl_3} RC{=}CHCOCH{=}CHCl.$$

The second way – a two-stage process – consisted in the condensation of acetylene with acid chlorides of α- or β-halo acids [cf. 4] and subsequent dehydrohalogenation of the 1- or 2-haloalkyl 2-chlorovinyl ketone formed; for example:

$$RCH_2CHXCOCl + CH{\equiv}CH \xrightarrow{AlCl_3} RCH_2CHXCOCH{=}CHCl \xrightarrow{-HX} RCH{=}CHCOCH{=}CHCl.$$

We used the first variant for the preparation of propenyl and 2-methylpropenyl 2-chlorovinyl ketones, in which crotonoyl and senecioyl chlorides, respectively, were condensed with acetylene. The reaction was carried out in carbon tetrachloride or dichloroethane solution under conditions similar to those used for the synthesis of alkyl 2-chlorovinyl ketones; it was accompanied by considerable resinification of the reaction mixture owing to the relative instability of the substance formed. However, after the usual treatment of the reaction mixture with ice, distillation gave propenyl and 2-methylpropenyl 2-chlorovinyl ketones in 35-50% yield.

In order to check the second possibility we investigated the condensation of acetylene with acid chlorides of α-bromo and α-chloro aliphatic acids. It was considered to be more expedient to use the bromo acids, owing to their greater accessibility, but several attempts to use them in the synthesis were made without success: condensation with acetylene in presence of aluminum chloride and subsequent dehydrobromination of the product gave a complex mixture of several substances, and this method was abandoned. The lack of success is probably to be explained by halogen exchange in the chlorovinyl group with the result that a difficultly separable mixture of the 2-chlorovinyl and 2-bromovinyl ketones is formed. This supposition appears to be well grounded, for exchange of the chlorine atom in alkyl 2-chlorovinyl ketones is well known [5].

The use of acid chlorides of α-chloro acids gave positive results. After trials with several methods of synthesizing these acids chlorides, Kharash's method [6] was found to be most convenient; this consists in the chlorination of acid chlorides with sulfuryl chloride in presence of catalytic amounts of iodine. After modifying the procedure somewhat, we were able to obtain acid chlorides of α-chloro acids in 40-60% yield.

Investigation of the condensation of acid chlorides of 2-chlorobutyric, 2-chloro-3-methylbutyric, and 3-chloropropionic acids with acetylene in carbon tetrachloride or dichloroethane at 10-15° showed that the usual treatment of the reaction mixture gave a mixture of two products – the corresponding 1- or 2-chloroalkyl 2-chlorovinyl ketone and the alkenyl 2-chlorovinyl ketone – the latter being obtained without a separate dehydro-

chlorination process. The elimination of hydrogen chloride from the chloroalkyl 2-chlorovinyl ketone that is formed in the first place evidently occurs in the reaction mixture itself, and it is known that, under certain conditions, aluminum chloride is a catalyst for the dehydrochlorination process [7]. Also, we regularly observed elimination of hydrogen halide during distillation. In this connection it must be pointed out that the readiness with which hydrogen chloride is eliminated is in some degree dependent on the structure of the corresponding chloroalkyl 2-chlorovinyl ketone. It is interesting that in one case – the condensation of 3-chloropropionyl chloride with acetylene – we succeeded in isolating both reaction products – 2-chloroethyl 2-chlorovinyl ketone and 2-chlorovinyl vinyl ketone – in the pure state by distillation. This result is not in accord with the earlier results of Yakubovich and Merkulova [8], who obtained only 2-chloroethyl 2-chlorovinyl ketone under these conditions. However, the separation is accompanied by considerable losses, and the method is not of preparative value for 2-chlorovinyl vinyl ketone. Under other conditions it is generally not possible to isolate both or one of the components of the mixture obtained by reaction of acid chlorides of α-chloro acids since distillation is always accompanied by elimination of hydrogen chloride and the distillate is always a mixture of the two substances. For our purpose there was no need to carry out the separation, and we subjected the mixture obtained by distillation to dehydrochlorination.

In spite of the difficulty to be expected in such operations, the selective elimination of hydrogen chloride without action on the chlorovinyl group was effected with the aid of diethylaniline, for even when distilled with such reagents alkyl 2-chlorovinyl ketones are not dehydrochlorinated [5]. The mixture of two products obtained by reaction of the acid chloride of a chloro acid with acetylene was heated with diethylaniline for one hour in a water bath. Diethylaniline hydrochloride was separated, and the alkenyl 2-chlorovinyl ketone was isolated by distillation. It must be stated here that a single treatment with diethylaniline is not always sufficient, a second treatment being necessary to remove a small residue of chloroalkyl 2-chlorovinyl ketone. It must be stated also that the use of dimethylaniline in this reaction does not give satisfactory results. By means of this two-stage method of synthesis we prepared 2-chlorovinyl vinyl ketone, 2-chlorovinyl propenyl ketone, and 2-chlorovinyl 2-methylpropenyl ketone in 30-50% yields.

As regards the comparative merits of the two methods described for the synthesis of alkenyl 2-chlorovinyl ketones, it should be noted that the direct method of synthesis from acid chlorides of α,β-unsaturated acids has the disadvantage that the latter are relatively inaccessible; in this case, however, pure alkenyl 2-chlorovinyl ketones are obtained directly. The second, two-stage method makes use of more accessible starting materials, but the procedure is more protracted and it is necessary to purify the reaction products carefully.

The alkenyl 2-chlorovinyl ketones are oily liquids, apart from 2-chlorovinyl propenyl ketone, which is a low-melting solid. All these compounds are unstable and rapidly darken in color, but they may be preserved several days in cold ethereal solution in presence of hydroquinone and in absence of light. 2-Chlorovinyl vinyl ketone has a marked tendency to polymerize; the reaction begins within several hours or, in ether solution, after one or two days. All alkenyl 2-chlorovinyl ketones have pungent odors and have a powerful effect on the mucous membrane and skin.

A notable feature in the chemical behavior of 2-chlorovinyl ketones is the high mobility of the chlorine atom [1]. It is interesting that, as far as can be judged from the characteristic reaction with 2-naphthol in hydrochloric acid in presence of ferric chloride [9], the mobility of chlorine in the new system, with its supplementary conjugation between the carbonyl group and the double bond of the alkenyl group, is not reduced. It was found that alkenyl 2-chlorovinyl ketones react like their saturated isologs, forming 3-(1-alkenyl)naphtho[2,1-b]pyrilium chloroferrates in high yields, a result which proves the structure of the compounds we obtained:

In this way we prepared pyrilium salts containing propenyl and 2-methylpropenyl radicals; these substances form dark-green crystals. 2-Chlorovinyl vinyl ketone also reacts with 2-naphthol, but the pyrilium salt formed rapidly undergoes further change, and we did not succeed in isolating it. The rate of this reaction when carried out under the usual standard conditions and the high yields of the pyrilium salts obtained give no reason to suppose that the mobility of the chlorine atom in alkenyl 2-chlorovinyl ketones is greatly different from the mobility of chlorine in alkyl-2-chlorovinylketones.

EXPERIMENTAL

2-Chlorobutyryl chloride. A mixture of 88 g of butyryl chloride, 119 g of sulfuryl chloride, and 1 g of iodine was boiled (90-110°) for 45-50 hours and then distilled, the fraction of b.p. 115-150° being collected. The product was shaken with mercury to free it from iodine and then distilled through a fractionating column of 10-15 theoretical plates. The fraction of b.p. 129-132° (756 mm), n_D^{20} 1.4475; and d_{17}^{4} 1.2360; was obtained in a yield of 70.0 g (80.3%).

2-Chloro-3-methylbutyryl chloride. This was prepared similarly from 147 g of 3-methylbutyryl chloride, 167 g of sulfuryl chloride, and 1 g of iodine. Similar treatment gave 110 g (58%) of a substance of b.p. 145.5-146.5° (749 mm).

2-Chlorovinyl vinyl ketone [1-chloro-1,4-pentadien-3-one]. A solution of 81 g of 3-chloropropionyl chloride [8] in 150 ml of carbon tetrachloride was introduced into a 500 ml three-necked flask fitted with stirrer, reflux condenser, and a tube through which a fairly gentle current of acetylene was passed. In the course of two hours 85 g of aluminum chloride was added, the temperature of the reaction mixture being kept below 10-15°. After acetylene had been passed for six hours, the mixture was decomposed by pouring it onto ice. The organic layer was separated, and the aqueous layer was extracted with chloroform. Solvent was vacuum-distilled from the combined extracts (bath temperature not above 50°), and vacuum-distillation of the residue gave 63 g of a substance of b.p. 50-92° (15 mm) which consisted of a mixture of 2-chlorovinyl ketone and 2-chloroethyl 2-chlorovinyl ketone. This mixture was treated with 65 g of freshly distilled diethylaniline, first at room temperature and then for one hour in a water bath. The mixture was cooled and diluted with 150 ml of ether. Diethylaniline was filtered off, and the ethereal solution was washed several times with 5% sulfuric acid and with water; it was then dried over sodium sulfate. Ether was distilled off, and distillation of the residue gave 21 g (31.5%) of 2-chlorovinyl vinyl ketone.* After being redistilled, the substance had the following constants: b.p. 48-49.5° (14 mm); n_D^{20} 1.4938; d_4^{20} 1.1274; found MR 30.07; calculated MR 29.23

Found %: C 51.29; 51.24; H 4.52; 4.41. C_5H_5OCl. Calculated %: C 51.54; H 4.32.

2-Chlorovinyl vinyl ketone is a slightly yellowish liquid of pungent odor which has a powerful action on the mucous membrane and skin. It rapidly turns into a dark-colored viscous mass, but it can be kept for some time in solution in ether containing hydroquinone.

2-Chlorovinyl propenyl ketone [1-chloro-1,4-hexadien-3-one]. 1. This was prepared similarly from 81 g of 2-chlorobutyryl chloride and 85 g of aluminum chloride in 200 ml of carbon tetrachloride, acetylene being passed for 7-8 hours at not above 15-20°. The fraction (57 g), b.p. 81-86° (15 mm), obtained after the usual treatment was a mixture of 2-chlorovinyl propenyl ketone and 1-chloropropyl 2-chlorovinyl ketone. It was treated with diethylaniline (51 g) as described above. Vacuum distillation gave 35 g (47.3%) of 2-chlorovinyl propenyl ketone, b.p. 70-72° (10 mm), which crystallized out completely in the receiver as a colorless crystalline mass, m.p. 38-39°.

2. The apparatus used was similar to that described above. Aluminum chloride (13.3 g) was added in small portions over a period of 15 minutes to a stirred, cooled (ice water) solution of 10.5 g of crotonoyl chloride in 50 ml of dichloroethane, and a stream of dry acetylene was passed in. Passage of acetylene was continued for 3.5 hours, and the temperature of the reaction mixture was not allowed to rise above 20-25°. The reaction mixture was poured onto ice, the aqueous layer was extracted twice with chloroform, and the organic layer combined with extracts was dried over calcium chloride. Solvent was vacuum-distilled off, and the residue was distilled, the fraction of b.p. 64-65° (7 mm) being collected. This solidified in the receiver to a crystalline mass, m. p. 37-39°. The yield was 6.5 g (50.5%).

2-Chlorovinyl propenyl ketone forms colorless crystals having a characteristic pungent odor.. It has a powerful action on the mucous membrane and skin.

Found %: C 54.94; H 5.57 . C_6H_7OCl. Calculated %: C 55.11; H 5.46.

2-Chlorovinyl propenyl ketone is soluble in organic solvents, but insoluble in water. It rapidly becomes dark-colored, but it can be kept for a long time in the dark as a solution in ether containing hydroquinone.

2-Chlorovinyl 2-methylpropenyl ketone [1-chloro-5-methyl-1, 4-hexadien-3-one]. 1. The procedure of Method 1 for the preceding compound was used. Acetylene was passed for seven hours at 15-20° through a solu-

* When a high-boiling fraction is present, it is necessary to give further treatment with diethylaniline in order to convert it into 2-chlorovinyl vinyl ketone.

tion of 60 g of 2-chloro-3-methylbutyryl chloride and 60 g of aluminum chloride in 150 ml of dichloroethane. The fraction (30 g), b.p. 78-92° (10 mm), obtained after the usual treatment was a mixture of 2-chlorovinyl 2-methylpropenyl ketone and 1-chloro-2-methylpropenyl 2-chlorovinyl ketone. It was treated with 32.5 g of freshly distilled diethylaniline by the above described method. Vacuum distillation gave 18.2 g (32.7%) of 2-chlorovinyl 2-methylpropenyl ketone, b.p. 76-79° (11 mm).

2. The procedure of Method 2 for the preceding compound was used. Acetylene was passed for 9 hrs. at not above 8-12° through a mixture 25 g senecioyl chloride [10], 75 ml of dichloroethane, and 32 g of aluminum chloride. The usual treatment and distillation gave 10.3 g (34%) of 2-chlorovinyl 2-methylpropenyl ketone, b.p. 71-73° (10 mm).

After being redistilled the 2-chlorovinyl 2-methylpropenyl ketone had the following constants: b.p. 71-73° (10 mm); n_D^{20} 1.5038; d_4^{20} 1.0644; Found MR 40.21; Calculated MR 38.47.

Found %: C 58.18; H 6.44. C_7H_9OCl. Calculated %: 58.16; H 6.28

2-Chlorovinyl 2-methylpropenyl ketone is a slightly yellowish liquid which has a powerful action on the mucous membrane and skin. It gradually darkens in color, but it can be kept a long time in the dark as a solution in ether containing hydroquinone.

Simultaneous preparation of 2-chloroethyl 2-chlorovinyl ketone [1,4-dichloro-1-penten-3-one] and 2-chlorovinyl vinyl ketone [1-chloro-1,4-pentadien-3-one]. Aluminum chloride (60 g) was added over a period of two hours with passage of acetylene into a mixture of 57.3 g of 3-chloropropionyl chloride and 120 ml of carbon tetrachloride contained in an apparatus similar to that described above. Passage of acetylene continued for seven hours in all, the mixture being stirred continuously and the temperature maintained below 20°. After the usual treatment and drying of the extracts, solvent was distilled off under reduced pressure (bath temperature not above 60°). Vacuum distillation of the residue gave a fraction (40.2 g) of b.p. 48-103° (15 mm). Two redistillations gave 10.1 g (17.7%) of 2-chlorovinyl vinyl ketone, b.p. 48-49° (15 mm) and n_D^{20} 1.5027 and 20.8 g (38.5%) of 2-chloroethyl 2-chlorovinyl ketone having the following constants: b.p. 100-102° (15 mm); d_4^{20} 1.2754 n_D^{20} 1.5045; Found MR 35.47, calculated MR 34.57. For 2-chloroethyl 2-chlorovinyl ketone the literature [8] gives b.p. 100-101° (15-16 mm).

2-Chloroethyl 2-chlorovinyl ketone is a colorless oil having a rather pungent odor. It can be kept in ethereal solution for a long time.

3-Propenylnaphtho[2,1-b]pyrilium chloroferrate. 2-Naphthol (2 g) and 12 ml of a solution of anhydrous ferric chloride in concentrated hydrochloric acid (prepared by dissolving 10 g of ferric chloride in 15 ml of concentrated hydrochloric acid) were added to a solution of 1.3 g of 2-chlorovinyl propenyl ketone in 20 ml of glacial acetic acid. The precipitate that formed after several hours was washed with a little glacial acetic acid and then with absolute ether. The yield was 2.8 g (67%). Recrystallization from glacial acetic acid gave fine dark-green crystals, m.p. 135-137° (with decomposition). This substance rapidly decomposes when kept, and for this reason we were unable to isolate it in an analytically pure state.

3-(2-Methylpropenyl)naphtho[2,1-b]pyrilium chloroferrate. This was prepared similarly from 0.7 g of 2-chlorovinyl 2-methylpropenyl ketone in 10 ml of glacial acetic acid, 1 g of 2-naphthol, and 6 ml of a solution of ferric chloride in concentrated hydrochloric acid. The yield was 1.5 g (71.5%). Recrystallization from glacial acetic acid gave fine dark-green crystals, m.p. 186-188°.

Found %: C 47.16; 47.35; H 3.30; 3.36 Fe 12.80; 12.69. $C_{14}H_{11}OCl_4Fe$. Calculated %: C 47.16; H 3.48; Fe 12.89.

SUMMARY

1. Two methods were developed for the synthesis of the previously unknown alkenyl 2-chlorovinyl ketones. The first method consists in the condensation of acid chlorides of α,β-unsaturated acids with acetylene in presence of aluminum chloride. The second method consists in the condensation of acid chlorides of α- and β-chloro acids with acetylene in presence of aluminum chloride and subsequent treatment of the reaction product with diethylaniline.

2. It was shown that alkenyl 2-chlorovinyl ketones react with 2-naphthol in presence of ferric chloride with formation of 3-(1-alkenyl)naphtho[2,1-b]pyrilium chloroferrates. This indicates the high mobility of chlorine in the alkenyl 2-chlorovinyl ketone molecule and proves the structure of these compounds.

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SYNTHESIS AND PROPERTIES OF (TRIPHENYLSILOXY)SILANES AND THEIR HYDROLYSIS PRODUCTS

V. S. Chugunov

In the literature [1,2] only a few branched organic polysiloxanes of the types $Si(OSiR_3)_4$ and $R_nSi(OSiR_3)_{4-n}$ have been reported, in spite of their ready formation by the condensation of silicon tetrachloride with the corresponding sodium trialkyl- and dialkylaryl-siloxides.

We considered it to be of interest to prepare compounds of this type containing only aryl radicals. With this object we took sodium triphenylsiloxide as starting material; at 0° in a benzene medium, this condensed with silicon tetrachloride or tetrafluoride according to the equation:

$$Ph_3SiONa + SiX_4 = Ph_3SiOSiX_3 + NaX.$$

It was shown that reaction of sodium triphenylsiloxide with excess of silicon tetrachloride proceeded smoothly with formation in 72% yield of trichloro(triphenylsiloxy)silane [1,1,1-trichloro-3,3,3-triphenyldisiloxane], m.p. 47-48°. When chlorine was eliminated by hydrolysis with 0.1 N NaOH and this was followed by removal of solvent under reduced pressure and heating at 150-160°, a clear glassy polymer was formed; this softened at 65-70° and had the empirical formula $[(C_6H_5)_3SiOSiO_{1.5}]_n$. When reaction was between equimolecular proportions of trichloro(triphenylsiloxy)silane and sodium triphenylsiloxide, a 53% yield of dichlorobis(triphenylsiloxy)silane [3,3-dichloro-1,1,1,5,5,5-hexaphenyltrisiloxane], m.p. 134-135°, was formed in accordance with the equation:

$$(C_6H_5)_3SiOSiCl_3 + (C_6H_5)_3SiONa = [(C_6H_5)_3SiO]_2SiCl_2 + NaCl$$

Hydrolysis with 1N NaOH gave bis(triphenylsiloxy)silanediol [1,1,1,5,5,5-hexaphenyl-3,3-trisiloxanediol], m.p. 168-169°

It was further shown that reaction between silicon tetrachloride and excess of sodium triphenylsiloxide in boiling benzene gave a 29.5% yield of chlorotris(triphenylsiloxy)silane [3-chloro-1,1,1,5,5,5-hexaphenyl-3-(triphenylsiloxy)trisiloxane]; its hydrolysis product – tris(triphenylsiloxy)silanol [1,1,1,5,5,5-hexaphenyl-3-(triphenylsiloxy)-3-trisiloxanol] – melts at 241-242°. It is interesting that sodium triphenylsiloxide reacts already in the cold with silicon tetrafluoride with formation of fluorotris(triphenylsiloxy)silane [3-fluoro-1,1,1,5,5,5-hexaphenyl-3-(triphenylsiloxy)trisiloxane], m.p. 230-231°; this again gives tris(triphenylsiloxy)silanol on hydrolysis.

Our attempts to attach a fourth triphenylsiloxy group to silicon by boiling fluorotris(triphenylsiloxy)silane with excess of sodium triphenylsiloxide in benzene were not successful.

EXPERIMENTAL

Trichloro(triphenylsiloxy)silane

a) A mixture of 27.6 g of triphenylsilanol dissolved in 250 ml of dry benzene and 4 g of sodium was prepared in a round-bottomed flask fitted with a reflux condenser and protected from influx of moisture. The mixture was boiled for three hours in order to complete the formation of sodium triphenylsiloxide, and it was then

cooled with ice water. A solution of 20 g of silicon tetrachloride in 100 ml of benzene was then added, and the mixture was boiled for two hours. Precipitated sodium chloride was filtered off. Fractionation of the filtrate gave 28.4 g (72%) of trichloro(triphenylsiloxy)silane, b.p. 256-260° (30 mm), m.p. 47-48°. The product was readily soluble in ether, benzene, and other organic solvents; it was rapidly hydrolyzed by atmospheric moisture.

Found %: Si 12.9; 13.2; Cl 26.7; 26.5 $(C_6H_5)_3SiOSiCl_3$. Calculated %: Si 13.6; Cl 25.9. Found: M 410; 415 Calculated M 409.8

b) When 20 g of trichloro(triphenylsiloxy)silane was treated with 0.1 N NaOH, a viscous rubber-like polymer was formed which was readily soluble in ether, acetone, and benzene. When solvent was removed at 150-160° (30-35 mm), 14.5 g of a slightly yellowish transparent glass-like polymer (softening point 65-70°) was obtained.

Found %: C 65.71, 65.57; Si 16.41; 16.35; H 4.73; 4.87. $[(C_6H_5)_3SiOSiO_{1.5}]_n$. Calculated %: C 66.0 Si 17.1; H 4.6.

c) A solution of 1.2 g of trichloro(triphenylsiloxy)silane in 50 ml of benzene was cooled to 0° and 100 ml of a solution of phenyllithium (prepared from 15.7 g of bromobenzene in 85 ml of ether and 1.4 g of lithium) was added. The mixture was boiled for two hours, and the complex was then decomposed with dilute hydrochloric acid. Recrystallization from benzene gave 0.96 g of hexaphenyldisiloxane, m.p. 220°, which is in accord with the reported value [3].

Dichlorobis(triphenylsiloxy)silane

Sodium triphenylsiloxide was prepared from 1.2 g of sodium and a solution of 5.5 g of triphenylsilanol in 100 ml of benzene. This solution was cooled, and 7.8 g of trichloro(triphenylsiloxy)silane diluted with 50 ml of benzene was added. After two hours at the boil, the precipitate of sodium chloride was filtered off. The filtrate was warmed slightly and concentrated to 30 ml by the passage of dry air. Crystals of dichlorobis(triphenylsiloxy) silane separated and were recrystallized from petroleum ether. The finely crystalline dichloro(triphenylsiloxy) silane, amounting to 7.2 g (53%), melted at 134-135°.

Found %: Si 12.4; 12.2; Cl 10.9; 10.6. $[(C_6H_5)_3SiO_2]SiCl_2$ Calculated %: Si 12.9; Cl 11.0. Found M 636 Calculated M 649.8.

Bis(triphenylsiloxy)silanediol

Dichlorobis(triphenylsiloxy)silane (3 g) was dissolved in 30 ml of ethanol, and 1N NaOH was added gradually until there was an excess to phenolphthalein. The precipitate formed was filtered off and recrystallized twice from benzene. The product, 2.4 g (90.2%) of colorless crystals, was bis(triphenylsiloxy)silanediol, m.p. 168-169°.

Found %: C 70.46; 70.31; Si 13.88; 13.53; H 5.30; 5.19. $[(C_6H_5)_3SiO_2]Si(OH)_2$. Calculated %: C 70.54; Si 13.74; H 5.27.

Chlorotris(triphenylsiloxy)silane

Sodium triphenylsiloxide was prepared as before from 2 g of sodium and 27.6 g of triphenylsilanol dissolved in 200 ml of benzene. Silicon tetrachloride (3.5 g) was then added to the solution, and the mixture was boiled for four hours. Sodium chloride was separated from the benzene solution, and chlorotris(triphenylsiloxy)silane was isolated from the filtrate as a finely crystalline powder. Two crystallizations from benzene gave 8.6 g (29.5%) of product, m.p. 219-220°. Chlorotris(triphenylsiloxy)silane is difficultly soluble in ether, but fairly readily soluble in warm benzene and toluene.

Found %: Si 12.6; 12.1; Cl 4.02; 4.08. $[(C_6H_5)_3SiO]_3SiCl$. Calculated %: Si 12.6; Cl 3.98. Found: M 856; 870 (cryoscopically in camphor). Calculated: M 889.6.

Tris(triphenylsiloxy)silanol

To a solution of 3.2 g of chlorotris(triphenylsiloxy)silane in 50 ml of a 1:1 mixture of benzene and ethanol, 20 ml of 3% potassium hydroxide solution was added. The mixture was boiled in a water bath for 30 minutes. After being washed free from alkali, the isolated product was recrystallized from benzene. The product, amounting to 2.2 g (70%), was tris(triphenylsiloxy)silanol, m.p. 241-242°.

Found %: C 74.52; 74.45; Si 12.52; 12.50; H 5.15; 5.27 $[(C_3H_5)_3SiO]_3SiOH$. Calculated %: C 74.43; Si 12.88; H 5.32

Fluorotris(triphenylsiloxy)silane

A benzene solution of sodium triphenylsiloxide was prepared from 27.6 g of triphenylsilanol, 200 ml of benzene, and 4 g of sodium, and gaseous silicon tetrafluoride, prepared by the action of sulfuric acid on a mixture of 15 g of sodium fluosilicate and 5 g of glass powder, was passed through this solution at room temperature. When silicon tetrafluoride ceased to be evolved, the sodium fluoride formed was filtered from the solution, which was heated to the boil. Fluorotris(triphenylsiloxy)silane was isolated as a finely crystalline powder and was recrystallized from benzene. The yield of product, m.p. 230-231°, was 22.6 g (77.4%).

Found %: Si 12.9; 12.6. $[(C_6H_5)_3SiO]_3SiF$. Calculated % Si 12.86. Found: M 862; 869 (cryoscopically in camphor). Calculated: M 873.3.

Fluorotris(triphenylsiloxy)silane (3 g) was treated with alkali under the conditions used for the hydrolysis of chlorotris(triphenylsiloxy)silane, and a 65% yield of tris(triphenylsiloxy)silanol was obtained and identified by its melting point.

SUMMARY

1. It was shown that sodium triphenylsiloxide reacts with silicon tetrachloride with successive attachment of one, two, and three triphenylsiloxy groups to silicon.

2. It was shown that the complete exchange of the halogens of silicon tetrafluoride and silicon tetrachloride by triphenylsiloxy groups does not occur when the silicon halide is treated with sodium triphenylsiloxide in boiling benzene; the reaction stops at halotris(triphenylsiloxy)silane.

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SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 6. PREPARATION OF SECONDARY DIALKYL(OR ARYL)CHLOROSILANES AND DIALKYL(OR ARYL)SILANOLS AND SOME OF THEIR REACTIONS

M. F. Shostakovsky, D. A. Kochkin, and V. M. Rogov

The preparation of dialkyl(or aryl)silanols having silicon-attached hydrogen (general formula R_2SiOH) and the derived disiloxanes $R_2Si(H)-O-Si(H)R_2$ has not been described in the literature. Such organosilicon compounds are of definite interest in view of their considerable reactivity and the possibility of using them as starting materials in organic synthesis.

The present paper describes the preparation of diethyl-, ethylisobutyl-, and ethylphenyl-silanols and their derivatives: symmetrical tetraethyl-, diethyldiisobutyl-, and diethyldiphenyl-disiloxanes; also the symmetrical tetraethyldisilazane $(C_2H_5)_2Si(H)-NH-Si(H)(C_2H_5)_2$. The starting materials for the preparation of the silanols were the corresponding dialkyl(or aryl)chlorosilanes: chlorodiethyl-, chloroethylisobutyl-, and chloroethylphenyl-silanes, which we prepared with the aid of organomagnesium and organolithium compounds. Apart from chlorodiethylsilane, the properties of which have not been adequately described, the preparation and properties of these compounds have not been described in the literature. They were synthesized from dichloroethylsilane $C_2H_5SiHCl_2$, which we prepared by the action of ethyl chloride on a mixture of copper and silicon at 260-270° [1].

We showed in a series of investigations [2-4] that trialkyl(or aryl)silanols react with vinyl ethers with formation of organosilicon acetals of structure $CH_3CH(OR'')(OSiR_3)$. Secondary (i.e. having silicon-attached hydrogen) dialkyl(or aryl)silanols also react with vinyl ethers with formation of acetals. In the present paper we describe the reaction of ethylisobutylsilanol with ethyl vinyl ether with formation of acetaldehyde ethyl ethylisobutylsilyl acetal:

$$C_2H_5(i\text{-}C_4H_9)SiHOH + CH_2{=}CHOC_2H_5 \rightarrow CH_3CH(OC_2H_5)(OSiH(C_2H_5)(i\text{-}C_4H_9))$$

Secondary dialkyl(or aryl)silanols are mobile liquids having a pungent camphor odor. They react with sodium or potassium with formation of crystalline siloxides:

$$R_2Si(H)OH + Na(K) \rightarrow R_2Si(H)ONa(K) + H$$

Secondary dialkyl(or aryl)silanols are less stable compounds than trialkyl(or aryl)silanols, for keeping for only a few hours at room temperature results in condensation with formation of the corresponding disiloxanes:

$$R_2Si(H)OH + HOSi(H)R_2 \rightarrow R_2Si(H)-O-Si(H)R_2 + H_2O$$

Of the dialkyl(or aryl)silanols that we prepared, the most stable was ethylisobutylsilanol, which condensed with formation of 1,3-diethyl-1,3-diisobutyldisiloxane only after being kept for a long time. The stabilities of our dialkyl(or aryl)silanols can be arranged in the series:

$$C_2H_5- < C_6H_5- < i\text{-}C_4H_9-.$$

We did not isolate diethylsilanol in the pure state, although we prepared it by two methods: a) hydrolysis of chlorodiethylsilane with 1 N NaOH:

$$(C_2H_5)_2Si(H)Cl + NaOH \rightarrow (C_2H_5)_2Si(H)OH + NaCl$$

and b) hydrolysis of 1,1,3,3-tetraethyldisilazane with aqueous hydrochloric acid:

$$2(C_2H_5)_2SiCl + NH_3 \rightarrow (C_2H_5)_2Si(H)-NH-Si(H)(C_2H_5)_2 + 2HCl \quad (1)$$

$$(C_2H_5)_2Si(H)-NH-Si(H)(C_2H_5)_2 + 2HOH \xrightarrow{HCl} 2(C_2H_5)_2Si(H)OH + NH_3 \quad (2)$$

It must be pointed out that the introduction of an isobutyl radical into the chlorosilane and silanol molecules greatly increases their stabilities. Thus it is much more difficult to hydrolyze an alkylchlorosilane containing an isobutyl radical, boiling for 5-6 hours with 1 N NaOH being required for complete hydrolysis. This behavior of these sterically hindered compounds is to be explained by higher electron density in the chloroethylisobutylsilane and ethylisobutylsilanol molecules. The compounds with silicon-attached hydrogen – dialkyl(or aryl)silanols and the corresponding disiloxanes and disilazanes – reduce silver nitrate solution to metallic silver and decolorize potassium permanganate solution.

Some physicochemical properties of dialkyl(or aryl)chlorosilanes, dialkyl(or aryl)silanols, and the corresponding disiloxanes are given in Tables 1 and 2.

EXPERIMENTAL*

Preparation of chlorodiethylsilane $(C_2H_5)_2Si(H)Cl$. A mixture of 24.0 g (1 mole) of magnesium turnings (or 14.0 g of lithium shavings **) and 200 ml of ether was prepared in a three-necked flask fitted with a reflux condenser protected by a calcium chloride tube, a dropping funnel, and a mechanical stirrer. Cooling was applied while 109.0 g of ethyl bromide was dropped in. The resulting ethereal solution of ethylmagnesium bromide was added from a dropping funnel to 129.8 g of dichloroethylsilane with stirring and cooling. The reaction mixture was then boiled for five hours. After separation of the ethereal solution of reaction products and its fractionation through a column, 55.0 g (44.8%) of a product of b.p. 97-99° (750 mm) was isolated, and this corresponded in analysis to chlorodiethylsilane.

Preparation of 1,1,3,3-tetraethyldisilazane $(C_2H_5)_2Si(H)-NH-Si(H)(C_2H_5)_2$. A solution of 40.8 g (0.3 mole) of chlorodiethylsilane in 300 ml of dry ether was prepared in a two-necked one-liter flask fitted with a tube for the passage of gas and a reflux condenser. The flask was placed in a water bath at 5°, and a stream of dry ammonia

* Junior scientific worker A. M. Gutman took part in the work.

** The reaction with lithium was carried out in a nitrogen atmosphere.

TABLE 1

Some Physicochemical Properties of Dialkyl(or aryl)chlorosilanes

No.	Name of alkylchlorosilane	Formula	B.p. in °C (p in mm).	d_4^{20}	n_D^{20}	Analysis for Cl (alkaline hydrolysis)		MR	
						found	calc.	found	calc.
1	Dichloroethylsilane	$C_2H_5Si(H)Cl_2$	74.5 (752)	1.0849	1.4129	55.00 54.18	55.0	29.64	29.80
2	Chlorodiethylsilane	$(C_2H_5)_2SiCl$ H	97—99 (750)*	0.8731	1.4114	26.25 27.00 23.20	27.50	34.90	34.80
3	Chloroethylisobutylsilane	$C_2H_5(C_4H_9\text{-}i)SiCl$ H	138—140.0 (750)	0.9829	1.4250	23.40	23.53	43.57	44.06
4	Chloroethylphenylsilane	$(C_2H_5)(C_6H_5)SiCl$ H	204.0—207.5 (746.5)	1.0505	1.5205	19.77 20.00	20.77	49.39	49.99

The literature [5] gives b.p. 99° (741 mm); b.p. 99-100° (760 mm).

was passed for four hours. With passage of ammonia a white precipitate formed and some heat was evolved. At the end of the reaction the ethereal solution was decanted from the precipitate of ammonium chloride and filtered. Ether was distilled off, and two fractionations of the residue gave 40.0 g (63.5%) of 1,1,3,3-tetraethyldisilazane, b.p. 102-103° (50 mm); 183-186° (170 mm); n_D^{20} 1.4340; d_4^{20} 0.8035; Found MR 61.42; Calculated for $C_8H_{23}Si_2N$, MR 61.01.

Found %: C 50.82; 50.95; H 12.16; 11.93; Si 29.18; 29.24; N 6.69; 6.70. $C_8H_{23}Si_2N$. Calculated %: C 50.72; H 12.29; Si 29.57; N 7.38.

Hydrolysis of 1,1,3,3-tetraethyldisilazane. The hydrolysis was carried out in the above-described apparatus. A mixture of 18.8 g (0.1 mole) of the tetraethyldisilazane, 130.0 ml of ether, 45 ml of water, and a few drops of methyl orange was prepared in the flask. This mixture was then stirred and cooled while 66.9 ml of 0.41 N HCl was added dropwise from the dropping funnel. The end of the reaction, which was detected by the change in color of the methyl orange, occurred after 3-4 hours. The ether layer was separated in a separating funnel and was dried with potassium carbonate. Fractionation gave the following products:

Fraction I, b.p. 49.5-51.6° (96.5 mm); n_D^{20} 1.4120; 4.8 g

Fraction II, b.p. 91.0-92.5° (50 mm); n_D^{20} 1.4140; 10.0 g

Fraction III, high-boiling products, 3.6 g

Refractionation of Fraction I gave 3.6 g (34.6%) of diethylsilanol, b.p. 50-52° (45.0 mm); n_D^{20} 1.4170; d_4^{20} 0.829; Found MR 31.61; Calculated MR 31.08. Diethylsilanol is a mobile liquid having a pungent camphor-like odor; it is of low stability. Refractionation of Fraction II gave 9.4 g of 1,1,3,3-tetraethyldisiloxane, a mobile colorless liquid without any specific odor. It is soluble in ether, benzene, dioxane, and other solvents, but insoluble in water; it can be distilled without decomposition, and it reduces silver nitrate solution and decolorizes potassium permanganate solution.

Preparation of 1,1,3,3-tetraethyldisiloxane $(C_2H_5)_2Si(H)\text{-}O\text{-}Si(H)(C_2H_5)_2$. The hydrolysis was carried out in the apparatus described above. A mixture of 49.2 g of chlorodiethylsilane, 200 g of ether, and a few drops of phenolphthalein

indicator was prepared in the flask. The reaction mixture was then stirred and cooled while 1N NaOH was added until a pink coloration occurred. The temperature of the reaction mixture did not rise above + 2°. The ethereal solution was separated from the aqueous layer and washed with water until neutral, ether was removed, and the residue was vacuum-fractionated from a Favorsky flask. The product, amounting to 25.0 g (80.1%) was 1,1,3,3-tetraethyldisiloxane.

Preparation of chloroethylphenylsilane $(C_2H_5)(C_6H_5)Si(H)Cl$. The procedure and apparatus were as described for chlorodiethylsilane. Fractionation of the products of reaction between 129 g of dichloroethylsilane and phenylmagnesium bromide prepared from 157 g of bromobenzene and 24 g of magnesium gave 95.6 g (56.0%) of chloroethylphenylsilane, b.p. 204-207.5° (746.6 mm); d_4^{20} 1.0805; n_D^{20} 1.5205. Chloroethylphenylsilane is a mobile fuming liquid having a camphor odor. It decomposes somewhat when distilled at atmospheric pressure, and when heated strongly or exposed to light it explodes. In some experiments the high-boiling reaction products also exploded when heated.

Hydrolysis of chloroethylphenylsilane. Hydrolysis was carried out with aqueous 1N NaOH as described above for the preparation of tetraethyldisiloxane. Vacuum fractionation of the hydrolysis products from 34.0 g (0.2 mole) of chloroethylphenylsilane gave the following fractions:

Fraction I, b.p. 43.5-46.0° (6.0 mm); n_D^{20} 1.5196; 7.0 g

Fraction II, b.p. 136-144° (3 mm), n_D^{20} 1.5252; 15 g

Redistillation of Fraction I gave 6.0 g (18.9%) of a product having b.p. 62.3-64.0° (19.5 mm), n_D^{20} 1.5090, d_4^{20} 0.9495, which corresponded in analysis to ethylphenylsilanol. Ethylphenylsilanol is a clear mobile liquid having an ethereal odor; on standing, it is readily converted into 1,3-diethyl-1,3-diphenyldisiloxane. It reacts with sodium even at room temperature. Refractionation of Fraction II gave 14.3 g of 1,3-diethyl-1,3-diphenyldisiloxane.

Preparation of 1,3-diethyl-1,3-diphenyldisiloxane $C_2H_5Si(H)(C_6H_5)-O-Si(H)(C_6H_5)C_2H_5$. A sealed tube containing 76 g (0.05 mole of ethylphenylsilanol was heated in a water bath for three hours. Distillation from a Favorsky flask gave 5.7 g (80.6 %) of product of b.p. 140.5° (3 mm), n_D^{20} 1.5250; and d_4^{20} 0.9884, which was found to be 1,3-diethyl-1,3-diphenyldisiloxane.

Preparation of chloroethylisobutylsilane $C_2H_5-Si(H)(i\text{-}C_4H_9)-Cl$. A mixture of 24 g of magnesium turnings, 300 ml of dry ether, and a few milliliters of ethyl bromide was prepared in a three-necked flask. With constant stirring and cooling, 137.03 g (0.1 mole) of isobutyl bromide (b.p. 91.5°, d_4^{20} 1.264; n_D^{20} 1.4346) was added. The isobutylmagnesium bromide was added to 129.0 g (1 mole) of dichloroethylsilane. Fractionation of the reaction products gave 70.5 g (46.7%) of a fraction of b.p. 140° (756 mm).

Found %: C 47.25; 47.13; H 9.99; 10.03; Si 17.96; 18.27; Cl 23.96; 23, 3; (titration with alkali) 23.20; 23.40. $C_6H_{15}SiCl$. Calculated %: C 47.82; H 10.03; Si 18.62; Cl 23.53.

The chlorine content of the chloroethylisobutylsilane was determined both by combustion and by boiling a weighed amount with 1N NaOH and back-titrating the unchanged alkali. It was shown that to combine all the determinable chlorine long boiling (5-6 hours) is required. The contents of Si, C, H, and Cl were determined by combustion of a sample in a quartz tube according to the procedure developed in the Microanalysis Laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

Preparation of Ethylisobutylsilanol $C_2H_5-Si(H)(i\text{-}C_4H_9)-OH$. Ethylisobutylsilanol was prepared by the hydrolysis of chloroethylisobutylsilane with 1N NaOH the apparatus and procedure being as for the experiment on the hydrolysis

TABLE 2

Some Physicochemical Properties of Dialky(or aryl)silanols and Corresponding Disiloxanes and Disilazanes.

Number	Name of substance	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Analysis C (%) found	Analysis C (%) calc.	Analysis H (%) found	Analysis H (%) calc.	Analysis Si (%) found	Analysis Si (%) calc.	MR found	MR calc.
	Silanols												
1	Diethylsilanol	$(C_2H_5)_2$ Si(H)OH	49.5—51.6 (96.5)	0.826	1.4140							31.08	31.52
2	Ethylisobutylsilanol	$(C_2H_5)(i\text{-}C_4H_9)Si(H)OH$	53—55 (9)	0.8237	1.4172	55.50 55.46	54.41	12.15 12.09	12.18	21.04 20.17	21.22	40.39	40.34
3	Ethylphenylsilanol	$(C_2H_5)(C_6H_5)Si(H)OH$	62.3—64.0 (19.5)	0.9695	1.5090	63.0 63.55	63.08	7.65 7.75	7.94	17.84 17.75	18.42	46.88	46.27
	Disiloxanes												
4	1,1,3,3-Tetraethyldisiloxane	$(C_2H_5)_2Si(H)-O-Si(H)(C_2H_5)_2$	92.2—92.5 (52.0)	0.8153	1.4154	50.02 50.10	50.45	11.51 11.61	11.64	29.56 29.86	29.47	58.52	58.70
5	1,3-Diethyl-1,3-diphenyldisiloxane	$C_2H_5(H)Si(C_6H_5)-O-Si(H)(C_2H_5)C_6H_5$	139.5—141 (4)	0.9884	1.5250	66.31 66.40	67.07	7.85 7.80	7.74	19.64 19.33	19.39	88.82	89.08
6	1,3-Diethyl-1,3-diisobutyldisiloxane	$C_2H_5(H)Si(i\text{-}C_4H_9)-O-Si(H)(C_2H_5)i\text{-}C_4H_9$	80,5 (11,5)—83,9 (12.5)	0.8099	1.4195	57.80 57.95	58.47	11.99 12.02	12.27	23.01 22.97	22.77	76.93	77.22
	Disilazanes												
7	1,1,3,3-Tetraethyldisilazane	$(C_2H_5)_2Si(H)-NH-Si(H)(C_2H_5)_2$	102—103 (50)	0.8035	1.4340	50.82 50.95	50.72	12.16 11.93	12.29	29.18 29.24	29.57	61.42	61.01

of chloroethylphenylsilane. Fractionation of the hydrolysis products from 30.1 g (0.2 mole) of chloroethylisobutylsilane from a Favorsky flask gave:

Fraction I, b.p. 70-76° (57.5 mm); n_D^{20} 1.4142

Fraction II, b.p. 126-136° (60.5 mm); n_D^{20} 1.4180

Fraction III, high-boiling products

Refractionation of Fraction I at a lower pressure gave 6.5 g (24.2%) of ethylisobutylsilanol, b.p. 53.0-55° (9 mm). Ethylisobutylsilanol is a colorless liquid having a camphor odor. It is soluble in ether, dioxane, and aromatic and aliphatic hydrocarbons. It reacts with sodium and potassium at room temperature.

Refractionation of Fraction II gave 9.6 g (34% calculated on ethylisobutylsilanol) of 1,3-diethyl-1,3-diisobutyldisiloxane; a clear mobile liquid of feeble odor. It can be distilled without decomposition, and it does not react with sodium or potassium at room temperature. B.p. 80.5° (11.5 mm) and 83.9° (12.5 mm).

Preparation of 1,3-diethyl-1,3-diisobutyldisiloxane $C_2H_5\underset{\underset{i\text{-}C_4H_9}{|}}{\overset{\overset{H}{|}}{Si}}-O-\underset{\underset{i\text{-}C_4H_9}{|}}{\overset{\overset{H}{|}}{Si}}C_2H_5$. A sealed tube containing 13.2 g of ethylisobutylsilanol (0.1 mole) and 1-2 drops of concentrated hydrochloric acid was heated in a boiling water bath for 2.5 hours. The reaction products were neutralized with potassium carbonate and fractionated. The product, amounting to 9.0 g (73.1%) was 1,3-diethyl-1,3-diisobutyldisiloxane.

Preparation of acetaldehyde ethyl ethylisobutylsilyl acetal. A mixture of 19.7 g (0.76 mole) of ethylisobutylsilanol, 10.8 g (0.75 mole) of ethyl vinyl ether (b.p. 36.5°; n_D^{20} 1.3760; d_4^{20} 0.7528), and one drop of concentrated hydrochloric acid was prepared in an ampoule cooled to a temperature of from − 3 to − 4°. The sealed ampoule was heated for five hours in a thermostat at 50-60°. The reaction products were treated with calcined potassium carbonate and then distilled from a Favorsky flask attached to a trap cooled in ice and salt. The following fractions were collected:

Fraction I, b.p. to 40° (760 mm); 7.2 g; n_D^{20} 1.4010

Fraction II, b.p. 100-106° (756 mm); 3.0 g; n_D^{20} 1.3810; d_4^{20} 0.8250

Fraction III, b.p. 178-181° (756 mm); 8.0 g; n_D^{20} 1.416; d_4^{20} 0.81388

Fraction IV, b.p. 85-101° (11 mm); 6.2 g; n_D^{20} 1.4220

Fraction V, high-boiling product – yellowish resin, 2.3 g

Fraction II contained the symmetrical diethyl acetal, for which the literature gives b.p. 103-104°; n_D^{20} 1.3820; d_4^{20} 0.8254.

Refractionation of Fraction III gave 4.5 g of a fraction of b.p. 181° (756 mm) and 98° (11 mm); this was found to be the ethyl ethylisobutylsilyl acetal, a clear mobile liquid having a pungent odor. It is soluble in ether, benzene, toluene, and aliphatic and aromatic hydrocarbons. Refractionation of Fraction IV gave 4.2 g of a fraction having b.p. 81.0° (9 mm), n_D^{20} 1.4190; and d_4^{20} 0.8099, which was found to be 1,3-diethyl-1,3-diisobutyldisiloxane. The structure of the acetal was confirmed by determining the acetaldehyde content of the hydrolysis products by the bisulfite method described previously [2].

The authors consider it their pleasant duty to express their thanks to members of the staff of the Microanalytical Laboratory, T. E. Shumilina and A. I. Guseva, for microanalytical determinations on the products synthesized.

SUMMARY

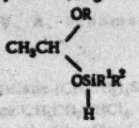
1. Dialkyl(or aryl)silanols containing silicon-attached hydrogen $R_2Si(H)OH$ and tetraalkyl(or aryl) disiloxanes of general formula $R_2\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Si}}-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{SiR_2}}$ were synthesized and characterized for the first time. Diethyl-,

ethylisobutyl-, and ethylphenyl-silanols and symmetrical tetraethyl-, diethyldiisobutyl-, and diethyldiphenyl-disiloxanes were prepared.

2. Chlorodiethyl-, chloroethylisobutyl-, and chloroethylphenyl-silanes were prepared for the first time.

3. It was shown dialkyl(or aryl)chlorosilanes (the example taken was chlorodiethylsilane) react with ammonia with formation of disilazanes $R_2Si-NH-SiR_2$. When hydrolyzed, 1,1,3,3-tetraethyldisilazane gives diethylsilanol and 1,1,3,3-tetraethyldisiloxane.

4. When dialkylsilanols react with vinyl ethers, organosilicon acetals of the following structure are formed:



(R^1 and R^2 are alkyl or aryl groups).

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OPTICAL INVESTIGATION OF TETRAETHYLSILANE AND CHLORO(ETHYL)SILANES AND THE BEHAVIOR OF THESE COMPOUNDS IN CHLORINATION

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1. Study of the chlorination of tetraethylsilane $(CH_3CH_2)_4Si$, chlorotriethylsilane $(CH_3CH_2)_3SiCl$, dichlorodiethylsilane $(CH_3CH_2)_2SiCl_2$, dichloroethylsilane $CH_3CH_2SiHCl_2$, and trichloroethylsilane $CH_3CH_2SiCl_3$ with chlorine in presence of ultraviolet radiation [1] and with sulfuryl chloride in presence of benzoyl peroxide [2] revealed interesting regularities in the relative ease with which the hydrogens of C–H bonds in these compounds are replaced by chlorine atoms. Whereas in the chlorination of tetraethylsilane practically only the hydrogen atom of the C–H bond in the α-position to silicon is replaced by chlorine, as the ethyl radicals of tetraethylsilane are replaced by chlorine atoms, the activity of the α-C–H bond in this respect is considerably reduced and the activity of the β-C–H bond is greatly increased, becoming predominant in $CH_3CH_2SiCl_3$; the Cl_3Si group of this compound has a very marked β-orienting effect.

The variation in this activity in the α- and β-C–H bonds can be expressed schematically as follows:

$(CH_3CH_2)_4Si$	activity	of the α-C–H bond	$\gg$	activity	of the β-C–H bond
$(CH_3CH_2)_3SiCl$	"	of the α-C–H bond	$>$	"	of the β-C–H bond
$(CH_3CH_2)_2SiCl_2$	"	of the α-C–H bond	$\approx$	"	of the β-C–H bond
$CH_3CH_2SiHCl_2$	"	of the α-C–H bond	$<$	"	of the β-C–H bond
$CH_3CH_2SiCl_3$	"	of the α-C–H bond	$\ll$	"	of the β-C–H bond

The above-noted orienting effect of the Cl_3Si group is found also in the chlorination of trichloropropylsilane $CH_2CH_2CH_2SiCl_3$ [3]; the relative amounts of trichloro(1-, 2-, and 3-chloropropyl)silanes are 1:3.5:3.1.

The present paper gives the results of a Raman-spectrum study of various peculiarities of the structures of tetraethylsilane and chloro(ethyl)silanes; it is these peculiarities that mainly determine the above-described regularities in the chlorination of these compounds.

The spectra of the above organosilicon compounds and of some corresponding hydrocarbons were determined on a Soviet three-prism spectrograph (ISP-51) with a central camera. The exciting radiation was the mercury line at 4358 A. The Raman spectra of tetraethylsilane, chloro(ethyl)silanes, trichloroethylmethane [1,2,3-trichloropropane], and other organosilicon compounds and hydrocarbons are given below.

1. $(CH_3CH_2)_4Si$. $\Delta\nu(cm^{-1})$: 170(3), 233(0), 264(2), 299(5), 332(db), 392(1), 549(10), 564(4), 636(3b), 690(0), 713(1*), 731(5*) 744(4*), 974(6), 1007(4), 1022(5), 1234(6), 1276(0), 1297(0), 1331(0), 1379(1), 1418(6), 1466(8), 2734(2), 2821(3*), 2879(10*), 2908(9*), 2940(4*), 2955(5*), 2968(0*).

2. $(CH_3CH_2)_2SiCl_2$. $\Delta\nu(cm^{-1})$: 168(3*), 219(2*), 242(1db), 281(sh), 301(4*), 316(4*), 325(1), 461(4*), 478(6*), 592(6**), 607(3**), 729(3*), 745(3*), 977(5), 1006(4*), 1024(4*), 1239(4), 1379(0), 1416(4), 1467(7), 2692(0), 2741(2), 2825(2), 2882(9*), 2914(6*), 2941(2*), 2968(4*), 2979(0*). (The lines 168-316 are on the background of the wing of the Rayleigh line).

3. $(CH_3CH_2)_2SiCl_2$. $\Delta\nu$[cm^{-1}]: 111(1*), 126(1*), 167(*), 185(5*b, db), 227(1**), 239(2**), 251(1**), 297(5*), 311(5*), 330(0), 420(0), 457(10*), 473(2*), 493(0), 531(2*), 548(2*), 615(5), 688(2*), 708(2*), 738(2**), 740(2**), 976(4), 1008(5*), 1024(2*), 1056(0), 1227(1*), 1242(5*), 1268(0), 1290(0), 1319(0db), 1400(5), 1433(0), 1463(6), 2741(1), 2825(2), 2885(8*), 2919(3*), 2934(4*), 2967(3), 2983(0). (The lines 111-185 are on the background of the wing of the Rayleigh line).

4. $(CH_3CH_2)SiHCl_2$. $\Delta\nu$[cm^{-1}]: 177(5), 188(5*), 226(0), 264(0), 296(4), 493(10 b), 548(3*), 566(3*), 660(5), 708(4), 709(5*), 813(5*), 975(3 db), 1010(3db), 1073(0), 1093(0), 1236(4), 1405(3), 1463(4), 2204(9 m), 2747(1), 2829(1), 2889(7), 2914(2*), 2938(4*), 2973(3**), 2986(1**). (The lines 177-296 are on the background of the wing of the Rayleigh line).

5. $(CH_3CH_2)SiCl_3$. $\Delta\nu$[cm^{-1}]: 120(4*), 166(2*), 179(9*), 193(0), 225(7), 325(7), 447(10), 564(4*), 580(4*), 717(4 b), 973(2*), 985(2*), 1015(4), 1222(1), 1244(4*), 1389(3*), 1425(2*), 1465(6), 2750(1), 2848(1), 2895(7*), 2931(2*), 2946(6*), 2978(3), 2996(0). (The lines 120-225 are on the background of the wing of the Rayleigh line, which extends beyond the line 225).

6. $(CH_3CH_2)_4C$. $\Delta\nu$[cm^{-1}]: 175(2), 371(3), 405(10), 457(1), 664(6), 682(7), 770(6 b), 800(0), 912(7), 1013(0), 1057(2), 1089(8*), 1102(0*), 1124(3*), 1151(4*), 1174(*), 1198(4*), 1229(4), 1272(6), 1308(1), 1350(3), 1383(3), 1458(10 m), 2734(2), 2826(2), 2864(3*sh), 2888(10*sh), 2922(9*), 2945(1*), 2964(4*).

7. $(CH_3CH_2)CCl_3$. $\Delta\nu$[cm^{-1}]: 177(0*), 192(5*), 244(5*), 271(5*), 332(5**), 343(3**), 408(10), 530(10), 697(4), 778(4), 829(3), 931(2), 1056(4*), 1090(1*), 1112(1*), 1271(2), 1430(4), 1458(4), 1497(0), 1522(0), 2744(1db), 2842(1), 2888(3*), 2943(10* db, b), 2961(3*), 2989(5*), 3009(0). (The lines 177-271 are on the background of the wing of the Rayleigh line).

Notes. Intensity is expressed on a ten-degree scale. Other indications given with the intensity are b - broad line; sh - sharp line; db - doublet; the asterisks denote lines occurring on a background that is common to neighboring lines marked with the same number of asterisks.

The spectrum of the first compound has been published previously [4]; it has recently been published in a more precise form [5]. Our results add some further precision to the latter publication with respect to the resolution of certain frequencies and the detection of some lines of low intensity.

The spectra of Compounds 2-5 were also published recently [6], but in an incomplete form (only in the region 160-1460 cm^{-1}). The region of valency vibrations of C-H bonds, which, as we shall see below, is very important for the solution of our problems, is not investigated at all in the investigation cited; moreover, this publication contains many inaccuracies and mistakes in the determination of frequencies, so that it is impossible to make use of these spectra.

Before their Raman spectra were determined, the compounds were distilled twice through a 35-plate column. In the case of the readily hydrolyzable chloro(ethyl)silanes, precautions were taken against the ingress of atmospheric moisture into the vessels in which the substances for investigation were collected in the distillation (i.e., the cells used for the determination of the Raman spectra). The compounds investigated had the following boiling points: $(CH_3CH_2)_4Si$, 152.5° (754.1 mm); $(CH_3CH_2)_3SiCl$, 146° (750.4 mm); $(CH_3CH_2)_2SiCl_2$, 129.7° (751.9 mm); $(CH_3CH_2)SiHCl_2$, 74° (744 mm); $(CH_3CH_2)SiCl_3$, 97.4° (749.3 mm); $(CH_3CH_2)_4C$, 144° (760 mm); $CH_3CH_2)CCl_3$, 107.0° (750 mm).

2. In investigations on the hydroxy group in various compounds, one of us [7] has shown that the protonization of its hydrogen atom (in acids) results in a definite reduction in the O-H bond energy, increase in the interatomic distance in this bond, and reduction in the hydroxyl vibration frequency. On the other hand, electronization of this bond (in a transition to an OH^- ion) reduces the interatomic distance, raises the bondenergy, and so raises the vibration frequency. The range of variation of the vibration frequency of the hydroxy group is considerable - from 2500 cm^{-1} for the β-form of crystalline oxalic acid to 4200 cm^{-1} for the OH^- ion; the range of variation of the other parameters of this bond that we have indicated is also very great.

The concept of the protonization and electronization of X–H bonds in the sense of a lesser or greater involvement of the proton in the electron-orbital system of the X–H bond can be applied also to C–H bonds [7], but the electronization of the C–H bond, unlike that of the O–H bond, is accompanied by the tendency to form an ion (CH^-); the carbon atom remains bound to the rest of the molecule, but the proton enters more deeply into the electron-orbital system of the C–H bond.

Protonization of the C–H bond again leads to a reduction in its vibration frequency, whereas electronization leads to an increase in this frequency; the range of variation of the vibration frequency and other parameters (energy, interatomic distance) of the C–H bond is much narrower in known compounds than for the hydroxy group. Thus, the vibration frequencies of the six C–H bonds of the two methyls of ethane lie in the range 2700-2960 cm^{-1}, the four C–H bonds of ethylene in the range 3000-3100 cm^{-1}, and the two C–H bonds of acetylene in the range 3300-3400 cm^{-1}. The following are the frequencies of the C–H bonds in these compounds [8]:

Frequencies of 6 C–H bonds in ethane (C–C):	2730(3), 2791(2 b), 2880(10), 2940(10), 2960(5)
Frequencies of 4 C–H bonds in ethylene (C=C):	(2988), 3008(10), 3074(2), (3107)
Frequencies of 2 C–H bonds in acetylene (C≡C):	(3288), 3372

Note: The frequencies in parentheses are infrared frequencies (cm^{-1}) [8].

3. In the ethyl radicals of the compounds that we have investigated there are two kinds of C–H bonds: one occurs in methyl groups, and the other in methylene groups of ethyl radicals.

As experimental [9] and calculated [10] data for paraffin hydrocarbons have shown, the CH_2 and CH_3 groups present are largely independent in the sense that interaction with other frequencies in the molecule and also interaction between methyl and methylene groups has little effect on the vibration frequencies of these groups. The truth of this statement is evidenced, for example, by the fact that lengthening of a carbon chain in the series of normal paraffins does not give rise to any change in the characteristic frequencies of the methylene and methyl groups; in intensity, however, the lines due to C–H bonds of methylene groups, unlike those due to methyl groups, increase, because the number of methylene groups increases with lengthening of the carbon chain, whereas there are only two methyl groups in normal paraffins.

On the basis of experimental data for unbranched paraffins and of approximate calculations of the frequencies of "isolated" CH_2 and CH_3 groups [9, 10], the methylene and methyl groups are each characterized by two vibrations – symmetrical and antisymmetrical – the Raman frequencies of which are (cm^{-1}):

	Symmetrical vibration	Antisymmetrical vibration (degenerate in CH_3)
CH_2	2853	2908
CH_3	2879	2967

In the spectra observed for unbranched paraffins there is also a frequency of 2938 cm^{-1} that is attributable to the CH_3 group, and there are one or two frequencies in the region of 2740 cm^{-1} the assignment of which has not been finally decided (it is possible that the frequencies 2938 and 2967 cm^{-1} result from the splitting of the degenerate CH_3 frequency on account of the disturbance of the symmetry of this group in complex molecules [9-11].

A fact of importance for the further discussion is the high intensity of the line due to the symmetrical vibration of the methyl group as compared with that of the line due to the symmetrical vibration of the methylene group. This may be directly observed in the case of n-butane ($H_3C \cdot CH_2 \cdot CH_2 \cdot CH_3$), in which there are two methyl and two methylene groups (intensities on the visual scale) [12]:

	Frequency (cm^{-1})	Intensity
CH_2	2861	10
CH_3	2878	15

This is evidenced also by data on the intensities of C–H lines of the methyl and methylene groups of normal paraffins recalculated for equal numbers of scattering molecules: the intensity of the line for the symmetrical vibration of the methylene groups of n-octane (there are six such groups) is substantially less than that of the line for the symmetrical vibration of the methyl groups (of which there are only two) [9].

It will be seen from the above-cited data on the methylene and methyl lines of normal paraffins that, although the regions of the frequencies of their C–H bonds generally overlap, we may nevertheless speak of the greater protonization of C–H bonds of methylene groups as compared with methyl groups, the C–H bonds of which are more electronized. Actually, the frequency of the symmetrical vibration of the methylene group (2853 cm^{-1}) is lower than that of the symmetrical vibration of the methyl group (2879 cm^{-1}), and the antisymmetrical vibration of the methylene group has a lower frequency (2908 cm^{-1}) than that of the antisymmetrical vibration of the methyl group (2967 cm^{-1}, or 2938 and 2967 cm^{-1} – see above).

4. It would be a great mistake, however, to attempt to extend these characteristics of the lines of the methylene and methyl groups of normal paraffins to the methylene and methyl groups of compounds of all kinds. It is clear that the only assertion that we can make which holds largely irrespective of the kind of molecule in which the groups occur, is that vibrations of the methylene and methyl groups are mutually independent. As regards the effect of the rest of the molecule, its manifestation in the frequency characteristics of the methylene and methyl groups is small only in the normal paraffins, but is considerable already in branched hydrocarbons, and still more so in compounds that are even more complex in composition and structure. As a result, in some compounds the regions of the methyl and methylene frequencies may be greatly displaced with respect to one another and the C–H bonds of one group may be more electronized or protonized relative to the bonds of the other; there will be corresponding changes in the chemical nature and reactivity of the C–H bonds of these groups.

Thus, in the spectra of the compounds $H_3Si-CH_2-SiH_3$ (one methylene group and no methyl groups) and $H_3Si-CH_2-CH_2-SiH_3$ (two methylene groups, no methyl groups), which we investigated previously [13], the frequencies of the methylene groups were greatly displaced in the direction of higher frequencies, which indicates powerful electronization: in these compounds the electron system is greatly displaced toward the carbon atoms, for, according to Gordy, the electronegativity of the carbon atom (2.55) is considerably greater than that of the silicon atom (1.8). In ketene [14] $H_2C=C=O$, the frequency region of the CH_2 group is displaced still further in the direction of the higher frequencies and lies considerably higher than the frequency regions of both methylene and methyl groups of normal paraffins, i.e. the CH_2 group of ketene is much more electronized than the methylene and methyl groups of normal hydrocarbons (see Table 1).

Hence, although the vibrations of the C–H bonds of methyl and methylene groups are independent of one another, their frequencies may be greatly displaced with respect to one another to an extent dependent on the structure of the rest of the molecule and the kinds of atoms it contains; such behavior is of course indicative of changes in interatomic distances, bond energies, and reactivity of the C–H bonds of these groups.

We now turn our attention to the results of the optical investigation of tetraethylsilane and chloro(ethyl)-silanes with the object of interpreting the regularities observed in the chlorination of these compounds.

5. Table 2 gives the five principal frequencies of the valency vibrations of the C–H groups of methyl and methylene groups from the Raman spectra of tetraethylsilane and three chloro(ethyl)silanes in which one, two, and three ethyls of the tetraethylsilane are replaced by chlorine atoms.

The number of the principal frequencies of the methyl and methylene groups of all these compounds remains constant, but their relative positions in the spectrum varies substantially. As regards the frequencies of the methyl groups of tetraethylsilane, they are almost identical with those of the methyl groups of normal paraffins – in particular, n-butane (cm^{-1}):

Frequencies of the methyl groups of	tetraethylsilane	2879	2940	2955
" " "	n-butane [12]	2878	2939	2956
" " "	tetraethylmethane	2888	2945	2964

Of the two frequencies of tetraethylsilane – 2955 and 2968 cm^{-1} – the methyl frequency is to be identified with 2955 cm^{-1}, as can be seen not only from the above comparison, but also from a comparison of intensities (see above): the third methyl line is much more intense than that of the antisymmetrical vibration of the methylene group (2968 cm^{-1}). The symmetrical vibration of the methylene group of tetraethylsilane has the frequency

TABLE 1

Frequencies of the Methyl and Methylene Groups of Various Compounds

Compounds	Frequencies (cm^{-1})						
CH_3 Normal paraffins	—	2879 (10)	—	—	2938 (8)	2967 (5)	--
CH_2 Normal paraffins	2853 (8)	—	—	2908 (2)	—	—	—
$H_3Si—CH_2—SiH_3$	—	—	2868 (0)	—	2941 (2)	—	—
$H_3Si—CH_2—CH_2—SiH_3$	—	—	2892 (10)	2911 (1)	—	—	—
$H_2C=C=O$	—	—	—	—	—	2052 (5)	3015 (4 b)

TABLE 2

Frequencies of Valency-bond Vibrations of the Methyl and Methylene Groups of Tetraethylsilane and Chloro(ethyl)silanes.

Compound	Frequencies (cm^{-1})				
	1	2	3*	4*	5
1. $(CH_3CH_2)_4Si$	2879(10)	2908(9)	2940(4)	2955(5)	2968(0)
2. $(CH_3CH_2)_3SiCl$	2882(9)	2914(6)	2941(2)	2966(4)	2979(0)
3. $(CH_3CH_2)_2SiCl$	2885(8)	2916(3)	2934(4)	2967(3)	2983(0)
4. $(CH_3CH_2)SiCl_3$	2895(7)	2931(2)	2946(6)	2978(3)	2978(0)
Rise in frequency from 1 to 4	+ 16	+ 23	+ 6*	+23*	+ 28
			14*		
	(CH_3)	(CH_3)	(CH_2)	(CH_2)	(CH_2)

* If we regard the frequencies in the third and fourth columns as the result of the splitting of the degenerate CH_2 frequency (see above), we may make a rough estimation of this last frequency (that which it would have were it not degenerate) for Compounds 1-4, namely 2948, 2954, 2951, 2962 cm^{-1}; the rise from 1 to 4 will be + 14 cm^{-1}.

2908 cm^{-1}, and its intensity (in accordance with the above discussion) is somewhat lower than that of the symmetrical vibration of the C—H bond of the methyl groups.

Hence, the methylene frequencies of tetraethylsilane, unlike the methyl frequencies, are very high as compared with the frequencies of the corresponding groups of normal paraffins in general and of n-butane (and also tetraethylmethane) in particular (cm^{-1}):

Frequencies of the methylene groups of	tetraethylsilane	2908	2968
" " "	n-butane [12]	2861	2910
" " "	tetraethylmethane	2864	2922

Also, the frequency of the symmetrical vibration of the methylene groups of tetraethylsilane (2908 cm^{-1}) is higher than that of the symmetrical vibrations of its methyl groups (2879 cm^{-1}), and the frequency of the antisymmetrical vibration of methylene groups (2968 cm^{-1}) is higher than those of the two remaining frequencies

of its methyl groups (2940, 2955 cm^{-1}). This means that, in contrast to the case of the normal paraffins, the C–H bonds of the methylene groups of tetraethylsilane are more electronized than the C–H bonds of its methyl groups; such bonds in tetraethylsilane, unlike those in normal paraffins, are the more protonized.

Such relative positions of the frequencies of the C–H bonds of methyl and methylene groups in the tetraethylsilane spectrum result from the influence of the central silicon atom. Its electronegativity (1.8) is considerably less than the electronegativities of the carbon (2.55) and hydrogen (2.13 atoms). As a result, the electronic system is drawn from the silicon atom onto the carbon and hydrogen of the C–H bonds of the methylene groups; the latter are electronized and the frequencies are greatly raised. This effect of the silicon atom does not pass on as far as the C–H bonds of the methyl groups, so that the methyl frequencies remain unchanged (it is possible that the enhanced electronization of the methylene groups screens the effect of the silicon atom on the methyl groups).

6. Replacement of one, two, and finally three ethyl radicals by chlorine atoms results in an increase in the frequencies of the C–H bonds not only of the methylene groups, but also of the methyl groups; in chloro(ethyl) silanes the more electronegative chlorine atoms (2.97) (both with respect to silicon atoms (1.88) and also to carbon (2.55) and hydrogen (2.13) atoms) draw to themselves the valency-electron system of the molecule – "compacts" it – and together with the electrons (more accurately, by means of them) it attracts also hydrogen nuclei. As a result the C–H bond energies are increased, the bond lengths are reduced, and the vibration frequencies of these bonds are raised. The methylene groups, being nearer to the chlorine atoms than the methyl groups, are the more strongly affected by the chlorine atoms; in fact (Table 2), from the first to the fourth compound the frequency of the symmetrical vibration of methyl C–H bonds rises by 16 cm^{-1} and the antisymmetrical vibration by 14 cm^{-1}, whereas the frequencies of the methylene C–H bonds increase by 23 and 28 cm^{-1} respectively. Both the methylene and methyl groups are electronized under the influence of the chlorine atoms, but the methylene groups are affected to much the greater extent.

7. The above considerations make it possible for us to make some approach toward an understanding of the regularities observed in the readiness with which the various hydrogens of the C–H bonds of tetraethylsilane and chloro(ethyl)silanes are replaced by chlorine atoms.

Chlorination proceeds with separation of hydrogen chloride. In the chlorination of tetraethylsilane the preferential replacement of the hydrogens of the α-C–H bonds by chlorine is favored by the following circumstances.

The chlorine molecule, which is somewhat polarized under the influence of the second reactant and of the fluctuation factor, proceeds, with its positive end foremost, toward the more electronized α-C–H bond of a methylene group. A chlorine atom seizes the hydrogen of this bond and separates in the form of hydrogen chloride. This capture evidently occurs by a radical mechanism: a proton with one electron is torn from the bond – not a bare proton, nor a proton with two electrons, for in these cases we should have an ionic mechanism. This assumption is justified by a consideration of the chlorination conditions – treatment with chlorine in presence of ultraviolet radiation or treatment with sulfuryl chloride in presence of benzoyl peroxide. However, we do not propose to discuss these questions in this paper, for supplementary data are required for their solution. The other atom of the chlorine molecule combines with the tetraethylsilane residue. The approach of the positive end of the chlorine molecule to the α-C–H bond is favored not only by the higher electronization of this bond, but also by the screening of the positive silicon nucleus by its large electron envelope; moreover, this large electron envelope contributes in itself to the attraction of the positive end of the chlorine molecule to the α-bond.

As the ethyl radicals are replaced by chlorine atoms, electronization of α-C–H bonds continues, but there is a simultaneous gradual disappearance of the additional α-directing effect of the silicon atom on the chlorine molecule. In fact, with the replacement of the first, second, and particularly third ethyl radical by chlorine, the silicon atom itself becomes strongly polarized and its electron envelope gathers together toward the chlorine atoms; as a result of such a powerful polarization of the molecule, the rather considerable positive charge of the silicon atom is "bared", which, particularly in trichloroethylsilane, does not permit the positive end of the chlorine molecule to approach α-C–H bonds; an effect in the same direction is exerted on the negative end of the chlorine molecule by the negative pole of the organosilane molecule, which is concentrated in the region of the chlorine atoms. As a result, the chlorine molecule moves away to the β-C–H bonds, which are adequately electronized, and chlorinates them by the same mechanism.

As a result of the same circumstances, in trichloropropylsilane ($CH_2CH_2CH_2SiCl_3$) the β-C–H and the γ-C–H are almost equally active with respect to the replacement of hydrogen by chlorine; the activity of the β-bonds is, however, somewhat higher (see above), which is probably due to their somewhat higher electonization in comparison with the more remote γ-bonds.

Chlorination of $CH_3CH_2SiHCl_2$ proceeds in a more complex fashion than that of other chloro(ethyl)silanes owing to the presence in this compound of a very reactive polarized Si–H bond, which is the first to be attacked by chlorine; the chlorine molecule again approaches this bond with its positive end foremost. At this stage of the reaction the main product is $CH_3CH_2SiCl_2$, and further reaction consists in the chlorination of this compound. A subsidiary direction of reaction is the chlorination of C–H bonds of the ethyl of $CH_3CH_2SiHCl_2$ without effect on the Si–H bond. In this case we have to consider the action of two chlorine atoms on the one remaining ethyl radical, so that the electronization of C–H bonds of methylene and methyl groups is enhanced, as compared with the case of $(CH_3CH_2)_2SiCl_2$. For this reason, with respect to degree of electronization of C–H bonds, in Table 2 $CH_3CH_2SiHCl_2$ should be placed between $(CH_3CH_2)_2SiCl_2$ and $CH_3CH_2SiCl_3$, since this compound has the following C–H frequencies:

in CH_2	2889(7)	–	2938(4)	2973(3)	–
in CH_3	–	2914(2)	–	–	2986(1)

This complex course of the chlorination of $CH_3CH_2SiHCl_2$ is supported by the fact that the compound $CH_3CH(Cl)SiHCl_2$, which still preserves an Si–H bond, can be isolated from the chlorination product.

8. The large electron envelope of the silicon atom – $1s^2$, $2s^2$, $2p^3$, $3s^2$, $3p^2$ – undoubtedly acts somewhat as a screen in chloro(ethyl)silanes and so reduces the above-described effects of the chlorine atoms on the electron system of the ethyl radicals. On the other hand, the low electronegativity of the silicon atom, in which respect it approaches Group IV metals [13], favors the above-noted extreme polarization of Si–Cl bonds and, particularly in $CH_3CH_2SiCl_3$, hinders the approach of the chlorine molecule to α-C–H bonds of methylene groups in the chlorination process.

In trichloroethylmethane $CH_3CH_2CCl_3$, the central atom is carbon, which has a much smaller electron envelope ($1s^2$, $2s^2$, $2p^3$) than the silicon atom; it therefore has a smaller screening action on the effect of chlorine atoms on the electron system of ethyl radicals. This circumstance results in greater electronization of the C–H bonds of methylene and methyl groups in $CH_3CH_2CCl_3$ than in $CH_3CH_2SiCl_3$. In particular, the frequencies of the α-C–H bonds of the methylene groups of $CH_3CH_2CCl_3$ lie in a very high region (2943, 3009 cm^{-1}), so that these bonds are highly activated with respect to the replacement of their hydrogens by chlorine.

On the other hand, owing to the more favorable ratio of the electronegativities of carbon and chlorine atoms (0.86) as compared with this ratio for silicon and chlorine (0.61), the C–Cl bonds in $CH_3CH_2CCl_3$ are not so greatly polarized as the Si–Cl bonds in $CH_3CH_2SiCl_3$. The repelling effect of the central carbon atom and its attached chlorine atoms on the chlorine molecule approaching α-C–H bonds of $CH_3CH_2CCl_3$ is therefore less than that of the central silicon atom and its attached chlorine atoms in $CH_3CH_2SiCl_3$.

These two substantial differences between $CH_3CH_2CCl_3$ and $CH_3CH_2SiCl_3$ clearly account for the fact that in the chlorination of the first compound replacement of hydrogen atoms by chlorine proceeds to a considerable extent in the α-C–H bonds of the methylene groups [15], and not predominantly in the β-C–H bonds of the methyl groups, as occurs in the second compound.

M. F. Zulina took part in the experimental optical work, and L. L. Mkhitaryan and A. D. Snegova assisted in the preparation of the substances for investigation.

SUMMARY

1. In the chlorination of tetraethylsilane, replacement of hydrogen by chlorine occurs predominantly in the C–H bonds of the α-methylene groups owing to their great electronization and to the screening of the positive charge of the silicon nucleus by its considerable electron envelope.

2. As the ethyl radicals of tetraethylsilane are successively replaced by chlorine atoms, there occurs increasing electronization of C–H bonds, both in methylene groups (to the greater extent) and in methyl groups; and the repelling action on the chlorine molecule also increases. As a result, in $CH_3CH_2SiCl_3$ chlorination already occurs preferentially at the β-C–H bonds.

3. The phenomena of electronization and protonization of bonds are important factors in the determination of the chemical behavior of matter, but they must always be considered in their relation to other factors of chemical structure and to the conditions of reaction.

LITERATURE CITED

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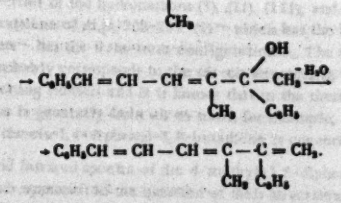
POLYENIC COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF 1,5-DIARYL-1,3,5-HEXATRIENES

B. M. Mikhailov and G. S. Ter-Sarkisyan

The reactions of organolithium compounds with α,β-unsaturated ketones have not received much study, and their reactions with ketones having two conjugated double bonds have received almost no study at all, in spite of the fact that the study of these latter reactions is of interest for the synthesis of difficultly accessible hexatrienes. Unlike organomagnesium compounds, which generally show both 1,2- and 1,4-addition to the conjugated systems of α,β-unsaturated ketones, organolithium compounds generally show only 1,2-addition, so that it is possible to pass from ketone to alcohols, and then further to hydrocarbons.

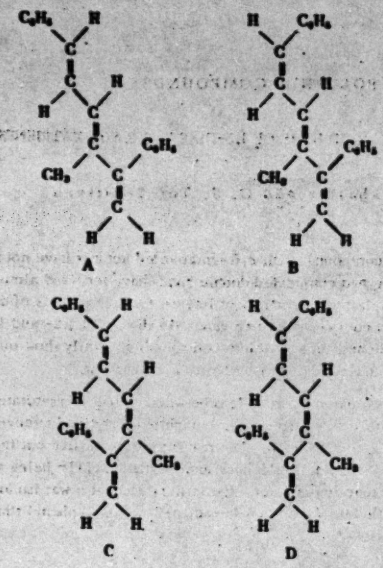
In the present work we have investigated the reactions between a doubly unsaturated ketone – 3-methyl-6-phenyl-3,5-hexadien-2-one – and aryllithiums (phenyl-, 1-naphthyl-, and 9-fluorenyl-lithiums) with the object of preparing aryl-substituted 1,3,5-hexatrienes. The reactions were carried out in ethereal solution, the hexadienone – prepared in good yield from cinnamaldehyde and 2-butanone [1] – being added to the organolithium compound. The intermediate reaction product – the tertiary alcohol – was isolated only in one case, namely in the reaction between 3-methyl-6-phenyl-3,5-hexadien-2-one with phenyllithium:



3-Methyl-2,6-diphenyl-3,5-hexadien-2-ol is a crystalline substance that does not melt sharply, probably because it is partially dehydrated when heated. By the dehydration of this substance under various conditions we succeeded in preparing the four theoretically possible isomers of 4-methyl-1,5-diphenyl-1,3,5-hexatriene. When 3-methyl-2,6-diphenyl-3,5-hexadien-2-ol was heated with acetic anhydride in presence of anhydrous sodium acetate, an almost quantitative yield was obtained of a mixture of two hydrocarbons of m.p. 202-203° (I) and 185-186.5° (II). Vacuum distillation of the alcohol gave two other hydrocarbons, one of them a solid, m.p. 92.5° (III), and the other a liquid (IV).

When the 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 92.5° was heated with acetic anhydride, it was converted into a mixture of the hydrocarbons of m.p. 202-203° and 185-186.5°; there can be no doubt, therefore, that the compounds (I), (II), and (III) are stereoisomers. As regards the geometric configurations of these hydrocarbons, the available data permit us to make only general observations.

The possible stereoisomers of 4-methyl-1,5-diphenyl-1,3,5-hexatriene A, B, C, and D differ among themselves in the disposition of the hydrogen atoms at one double bond and in the disposition of the extreme double bonds relative to the central double bond:



In conformity with the properties of the hydrocarbons (I), (II), (III), and (IV), it may be supposed that the 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 202-203° (I) – which has the highest melting point and the lowest solubility in organic solvents – has the trans-trans configuration A. The configuration of the readily soluble hydrocarbon of m.p. 92.5° (III) probably corresponds to the cis-cis structure D, for this hydrocarbon is converted by heat into a mixture of high-melting isomers and it is known that in the thermal isomerization of substances of similar structure the transformation is generally from cis to trans; for example, when heated, cis-stilbene is converted into trans-stilbene [2] and cis-cis-1,4-diphenyl-1,3-butadiene is converted into the trans-trans isomer [3].

A study of the ultraviolet and infrared spectra of the 4-methyl-1,5-diphenyl-1,3,5-hexatriene isomers will probably enable us to make a closer approach to the question of their structures. It must be pointed out that the question of the stereoisomerism of aryl-substituted hydrocarbons has received little attention in the literature. Lunde and Zechmeister [4] found that, under certain conditions, 1,6-diphenyl-1,3,5-hexatriene can be converted into a mixture of isomeric hydrocarbons, of which only one was isolated in the pure state by the authors. Koelsch and Richter [5] state that two hydrocarbons that they prepared, m.p. 172-174° and 203-206°, were probably stereoisomers of 1,1,6,6-tetraphenylhexatriene.

In the reaction between 3-methyl-6-phenyl-1,3-hexadien-2-one and 1-naphthol we were unable to isolate the tertiary alcohol. Heating of the reaction product with acetic anhydride gave only one hydrocarbon, which corresponded in composition to 4-methyl-5-(1-naphthyl)-1-phenyl-1,3,5-hexatriene.

In reaction with 3-methyl-6-phenyl-3,5-hexadien-2-one, 9-fluorenyllithium reacts quite differently from phenyllithium and 1-naphthyllithium. In this case the substance isolated as the main product was not the tertiary alcohol, but an unsaturated ketone, which gave reactions characteristic for the carbonyl group. The formation of a ketone instead of an alcohol indicates that the addition of 9-fluorenyllithium to 3-methyl-6-phenyl-3,5-

hexadien-2-one differs from the usual 1,2-addition of organolithium compounds to unsaturated ketones and occurs either in the 1,4- or 1,6-positions, since there are two double bonds in the ketone under investigation.

It should be noted that several cases of the 1,4-addition of 9-fluorenyllithium to α,β-unsaturated ketones have been observed by Tucker and Whalley [6]. The reaction of 9-fluorenyllithium with ketones having two conjugated double bonds has not been studied previously.

In order to resolve the question of whether the reaction between 9-fluorenyllithium and 3-methyl-6-phenyl-3,5-hexadien-2-one proceeds through 1,4- or 1,6-addition, the unsaturated ketone that we obtained was subjected to ozonization. Acetic acid was isolated from the products, but no benzoic acid was obtained. A compound was obtained, in the form of its 2,4-dinitrophenylhydrazone, from the neutral products of the reaction, and in elementary composition this corresponded to the 2,4-dinitrophenylhydrazone of β-phenyl-9-fluorenepropionaldehyde. These results indicate that 9-fluorenyllithium undergoes 1,6-addition with 3-methyl-6-phenyl-3,5-hexadien-2-one, and the ketone then obtained is 6-(9-fluorenyl)-3-methyl-6-phenyl-3-hexen-2-one.

EXPERIMENTAL

3-Methyl-2,6-diphenyl-3,5-hexadien-2-ol. Over a period of 45 minutes, an ethereal solution of 17.3 g (0.093 mole) of 3-methyl-6-phenyl-3,5-hexadien-2-one [1] was added to an ethreal solution of phenyllithium prepared from 16 g of bromobenzene and 1.42 g of lithium. The reaction mixture was boiled for three hours, and on the next day it was decomposed with water. The ether layer was separated and dried, and the ether was distilled off. The residual viscous oil crystallized out on addition of ethanol. The precipitate was filtered off, washed with a little alcohol, and dried in a vacuum desiccator (19 g; m.p. 70-101°). A further 2.1 g of precipitate of m. p. 68-99° was isolated from the mother liquor. The yield of 3-methyl-2,6-diphenyl-3,5-hexadien-2-ol was 86%. After being crystallized from ethanol, aqueous methanol, or benzene, the substance was obtained in the form of white needles, m.p. 68-85°.

When vacuum-distilled, the crystalline alcohol was partially dehydrated. The fraction of b.p. 220-223° (8 mm) had the following elementary composition:

Found %: C 87.78; 87.84; H 7.63; 7.55. $C_{19}H_{20}O$. Calculated %: C 86.32; H 7.63.

4-Methyl-1,5-diphenyl-1,3,5-hexatriene stereoisomers of m.p. 203° (I) and 186.5° (II). A solution of 5 g of 3-methyl-2,6-diphenyl-3,5-hexadien-2-ol in 25 ml of acetic anhydride was boiled for 15 hours with 3 g of anhydrous sodium acetate. The reaction mixture was then poured into water. The precipitate that formed was filtered off and dried in a vacuum desiccator. The product, amounting to 4.5 g, was a yellow crystalline substance, m.p. 143-167°. The yield of the mixture of hydrocarbons (I) and (II) was almost quantitative. When 1.4 g of the substance was crystallized from a 1 : 2 mixture of ethanol and benzene, a white substance (0.44 g) of m.p. 187-196° was obtained; crystallization of this from benzene and then from glacial acetic acid gave 4-methyl-1,5-diphenyl-1,3,5-hexatriene (I) in the form of fine white rhombs, m.p. 202-203°; the substance is of low solubility in alcohols.

Found %: C 92.73; 92.68; H 7.38; 7.44. $C_{19}H_{18}$. Calculated %: C 92.68; H 7.32.

Dilution of the main mother solution with ethanol gave 0.47 g of white crystals, m.p. 170-181°, and repeated recrystallization of these from glacial acetic acid gave gleaming white crystals of 4-methyl-1,5-diphenyl-1,3,5-hexatriene (II), m.p. 185-186.5°. In admixture with the 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 202-203°, this substance melted at 169-178°.

Found %: C 92.85; 92.73; H 7.31; 7.33. $C_{19}H_{18}$. Calculated %: C 92.68; H 7.32.

4-Methyl-1,5-diphenyl-1,3,5-hexatriene isomers (III) and (IV). The oil (23.5 g) obtained as described above from 18.6 g (0.1 mole) of 3-methyl-6-phenyl-3,5-hexadien-2-one and phenyllithium was vacuum-distilled without first isolating the tertiary alcohol as a solid. The fractions obtained were:

Fraction I, b.p. 200-230° (14 mm); 5.25 g
Fraction II, b.p. 230-240° (14 mm); 8.0 g
Fraction III, b.p. 240-250° (14 mm); 2.25 g
Residue 5.5 g

Fraction I partially crystallized out. The crystals (1.75 g, m.p. 68-75°) were separated from the oil and recrystallized from methanol; 0.9 g of substance of m.p. 87-91° was obtained. When ether was added to Fraction II (a viscous oil), a further 1 g of substance of m.p. 87-91° was isolated. Recrystallization of this substance from methanol gave white plates, m.p. 92-92.5°; this substance – 4-methyl-1,5-diphenyl-1,3,5-hexatriene (III) – is readily soluble in organic solvents.

Found %: C 92.57; 92.65; H 7.52; 7.46. $C_{19}H_{18}$. Calculated %: C 92.68; H 7.32.

Redistillation of Fraction II (after separation of the hydrocarbon of m.p. 92.5°) gave 1.5 g of a light-yellow liquid, b.p. 170-173° (3 mm), n_D^{22} 1.6243. This, according to analysis, was 4-methyl-1,5-diphenyl-1,3,5-hexatriene.

Found %: C 92.51; 92.55; H 7.48; 7.45. $C_{19}H_{18}$. Calculated %: C 92.68; H 7.32. Found: M 242; 251. Calculated: M 246.33.

Isomerization of 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 92.5°. a) A solution of 0.5 g of 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 92.5° in 2.5 ml of acetic anhydride was boiled with 0.3 g of anhydrous sodium acetate for 15 hours. The reaction mixture was poured into water, and the precipitate that formed was filtered off. The precipitate (0.43 g; m.p. 142-167°) was crystallized from a mixture of ethanol and benzene, and then from glacial acetic acid, as indicated above. The products isolated were 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 196-200° (undepressed by admixture of the hydrocarbon (I) obtained previously) and 4-methyl-1,5-diphenyl-1,3,5-hexatriene of m.p. 181-185° (undepressed by admixture of the hydrocarbon (II) obtained previously).

b) It was found that 4-methyl-1,5-dipheny-1,3,5-hexatriene of m.p. 92.5° underwent the same transformation into two isomeric hydrocarbons when it heated for four hours at 150-155°.

4-Methyl-5-(1-naphthyl)-1-phenyl-1,3,5-hexatriene. An ethereal solution of 14.9 g (0.08 mole) of 3-methyl-6-phenyl-1,3-hexadien-2-one was added over a period of 40 minutes to an ethereal solution of 1-naphthyllithium prepared from 19 g of 1-bromonaphthalene and 1.28 g of lithium. The reaction mixture was boiled for four hours, and on the next day it was decomposed with water. The usual treatment and removal of ether gave a dark-brown viscous oil (23.5 g), from which naphthalene was removed by steam-distillation and the residual solid resin was extracted with hot ethanol. When the alcoholic solution was cooled, perylene crystallized out (0.1 g; m.p. 272-275°). After removal of alcohol the residual resin-like solid (13.6 g) was dehydrated with acetic anhydride under the conditions described above. The product (12.8 g) was a dark-colored powder, m.p. 60-105°; crystallization of this from a 1 : 1 mixture of ethanol and ethyl acetate gave 2.9 g of white crystals, m.p. 219-225°, yield 12%. After being recrystallized from ethyl acetate and then from a mixture of benzene and ethanol, 4-methyl-5-(1-naphthyl)-1-phenyl-1,3,5-hexatriene formed very small white crystals, m.p. 230-231°.

Found %: C 93.21; 93.23; H 6.79; 6.83. $C_{23}H_{20}$. Calculated %: C 93.20 H 6.80.

6-(9-fluorenyl)-3-methyl-6-phenyl-3-hexen-2-one. An ethereal solution of 13 g (0.07 mole) of 3-methyl-6-phenyl-3,5-hexadien-2-one was added over a period of 45 minutes to an ethereal solution of 9-fluorenyllithium prepared from 12.8 g (0.077 mole) of fluorene and phenyllithium. The reaction mixture was boiled for two hours, and on the next day it was decomposed with water. After the usual treatment and removal of ether, there remained a red oil (27.5 g), from which a crystalline precipitate formed when methanol was added. The yield of crystals, m.p. 98-101°, was 10.6 g (43%). After being twice recrystallized from ethanol, 6-(9-fluorenyl)-3-methyl-6-phenyl-3-hexen-2-one was obtained as white plates, m.p. 102-103.

Found %: C 88.38; 88.42; H 6.83; 6.82. $C_{26}H_{24}O$. Calculated %: C 88.60; H 6.86.

The 2,4-dinitrophenylhydrazone of this ketone was prepared in ethanol solution in presence of traces of concentrated hydrochloric acid; it was obtained as orange-yellow crystals, m.p. 153-155°.

Found %: C 72.03; H 5.25; N 10.74. $C_{32}H_{28}N_4O_4$. Calculated %: C 72.19; H 5.30; N 10.53.

The residue remaining after the removal of solvent from the main mother liquor was fractionally distilled, and subsequent crystallization gave fluorene (3.1 g), difluorenylethane (0.65 g), m.p. 242-243°, and a hydrocarbon (0.3 g), m.p. 143-156°, the composition of which differed from that of 1-fluorenyl-2,3-dimethyl-6-phenyl-1,3,5-hexatriene.

Found %: C 93.99; H 5.85. $C_{33}H_{32}$. Calculated %: C 93.37; H 6.83.

Ozonization of 6-fluorenyl-3-methyl-6-phenyl-3-hexen-2-one. A solution of 5 g of the ketone in 30 ml of dry chloroform was ozonized for 11 hours with oxygen containing 6% of ozone. After the usual treatment, 0.5 g of acetic acid, b.p. 115-118°, was isolated from an acid medium. The 2,4-dinitrophenylhydrazone of 5-phenyl-5-fluorenepropionaldehyde was prepared from the neutral ozonization products (4 g of a viscous yellow oil), and after being recrystallized several times from glacial acetic acid, it melted at 225-227°.

Found %: C 69.56; H 4.61; N 11.65. $C_{28}H_{22}N_4O_4$. Calculated %: C 70.28; H 4.63; N 11.71.

The neutral ozonization products yielded also the 2,4-dinitrohydrazone of 9-fluorenone, m.p. 290°, undepressed by admixture of synthesized fluorenone 2,4-dinitrophenylhydrazone.

SUMMARY

1. Phenyllithium and 1-naphthyllithium undergo 1,2-addition to the conjugated system of 3-methyl-6-phenyl-3,5-hexadien-2-one with formation of the corresponding tertiary alcohols, which give arylhexatrienes by further reaction. On the other hand, 9-fluorenyllithium undergoes 1,6-addition with this ketone with formation of the unsaturated ketone 6-fluorenyl-3-methyl-6-phenyl-5-hexen-2-one.

2. By the dehydration of 3-methyl-2,6-diphenyl-3,5-hexadien-2-ol, four stereoisomeric 4-methyl-1,5-diphenyl-1,3,5-hexatrienes can be prepared.

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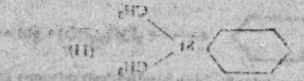
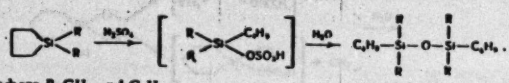


REACTION OF SILACYCLOPENTANES AND SILACYCLOHEXANES WITH CONCENTRATED SULFURIC ACID

A. F. Plate, N. A. Belikova, and Yu. P. Egorov

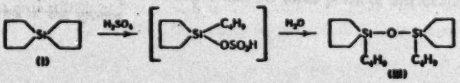
We have shown previously [1] that concentrated sulfuric acid opens the rings of silacyclopentanes quantitatively at the Si–C bond. When the sulfuric ester that is formed at first is treated with water, a disiloxane is obtained in 94% yield:



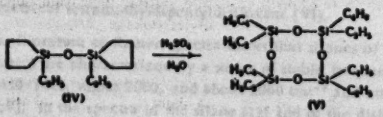
where R=CH_3 and C_2H_5

The methyl or ethyl group is not eliminated. In the present investigation we have shown that this reaction can be extended to other cyclic systems containing silicon as a hetero member of the ring, namely, bistetramethylenesilane (I) – a spiran containing two five-membered rings – and the silacyclohexane compound dimethyl(pentamethylene)silane (II).

In the case of the spiran (II) reaction proceeds just as readily as with other silacyclopentanes, but under the given conditions only one ring is broken and the dibutylbistetramethylenedisiloxane (III) is obtained in 90% yield:

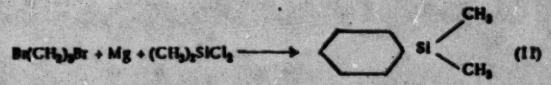


The higher stability of the five-membered ring in the sulfuric ester derivative formed is probably to be explained by the presence of an Si–O bond, which stabilizes the Si–C bond in the ring. However, under more severe conditions, this ring is also opened, this being shown for the case of diethylbistetramethylenedisiloxane (IV), which we prepared previously. When the usual excess of sulfuric acid was increased tenfold and the treatment after decomposition with water was made more prolonged, this disiloxane yielded a new cyclic siloxane – symmetrical tetrabutyltetraethylcyclotetrasiloxane (V):



Thus, on the basis of five examples, it was shown that silacyclopentanes react with sulfuric acid with quantitative scission of the ring at the Si–C bond.

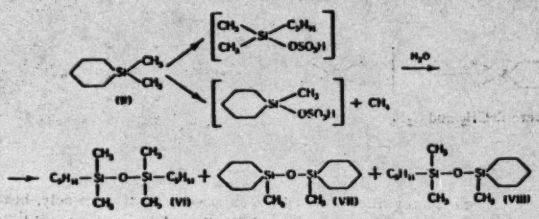
The silacyclohexane dimethyl(pentamethylene)silane (II) was prepared in 26.7% yield by the reaction:



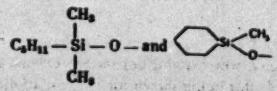
It reacts differently with concentrated sulfuric acid. Reaction proceeds in two directions: with scission of the six-membered ring at the Si–C bond, and with elimination of methyl group from the silicon atom. Moreover, these two reactions proceed at the same rate, as can be judged from the amount of methane evolved. However, the rate at which the six-membered cycle reacts with sulfuric acid is about one-twentieth of the rate of five-membered cycles, which indicates the higher stability of the six-membered silicon-containing ring under the given conditions.

This new interesting reaction, in which a methyl group is eliminated from a silicon atom under the action of sulfuric acid, was known for organosilicon compounds containing a functional group [of the type $(CH_3)_3Si(CH_2)_nX$] [2], but was not known for aliphatic hydrosiliconcarbons.

Hence, as a result of scission with sulfuric acid, a mixture of equal amounts of two sulfuric esters is obtained, and by treatment with water these can give three different siloxanes (VI), (VII), and (VIII):



We did not succeed in separating this mixture into its components owing to the closeness of the boiling points of these siloxanes. Chromatography on silica gel also failed to separate them. Of the disiloxanes that can be formed in this reaction, only (VII) has been described [3]. In order to determine the composition of the mixture obtained, we specially synthesized the siloxane (VI). From a comparison of the physical constants of the siloxanes (VI) and (VII) (including molecular refraction) and from analysis and determinations of molecular weight and the amount of methane evolved in the reaction, it may be assumed that all three possible disiloxanes are present in the reaction mixture and the contents of the groups



in the mixture are equal.

In order to confirm these results on the composition of the mixture we made use also of Raman spectra obtained, on the one hand, for the mixture of disiloxanes and, on the other hand, separately for dimethyl(pentamethylene)silane (II) and symmetrical tetramethyldipentyldisiloxane (VI).

A comparison of data in the literature on Raman spectra shows that silanes of the structures $(CH_3)_3SiR$ and $(CH_3)_2SiRR'$ (R and R' being aliphatic) are characterized by a series of stable frequencies lying in the regions 680-705, 830-840, 1250-1262, 1410-1415, about 2900, and about 2960 cm^{-1} and attributable to vibrations in CH_3 groups attached to silicon [4, 5]. In the spectra of the silane (II) and of the disiloxane (VI), which are given below, these frequencies are indeed found: the silane (II) gives 694, 833, 1251, 1408, 2900, and 2965 cm^{-1}, and

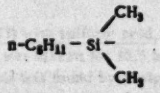
the disiloxane (VI) gives 705, 838, 1268, 1410, 2904 and 2965 cm^{-1}. It is found that characteristic frequencies are to be attributed to other aliphatic radicals attached to silicon, e.g. C_3H_9, C_3H_7, C_4H_9, and C_5H_{11}, the most characteristic being four frequencies, which are displaced in a regular fashion as the chain is lengthened [5]. Thus for silicon-attached C_3H_9, the following frequencies are always observed: 972-978, 1010-1020, 1230-1240, and 1460-1470 cm^{-1}, of which the first two are to be attributed to valency vibrations ν (C–C) and the last two to deformational vibrations δ (C–H). With lengthening of the chain to C_5H_{11}, the first two are raised to about 1030 and about 1067 cm^{-1}, and the second two are lowered to 1200 and 1455 cm^{-1}. With further lengthening of the chain this process is continued to 1050, 1080 cm^{-1} and 1192, 1445 cm^{-1} for C_6H_9 and about 1070, about 1100 cm^{-1} and 1185, 1440 cm^{-1} for C_8H_{11}. In the spectrum of the disiloxane (VI) such frequencies can indeed be found: 1070, 1102, 1186, and 1443 cm^{-1}.

It must be pointed out that the Raman spectrum of the silane (I) contains the same set of frequencies as that indicated in our paper [6] as characteristic for a five-membered ring containing silicon; in the silane (I) the intensities of these lines are almost double. In the spectrum of the silane (II), apart from the frequencies due to the CH_3 groups attached to silicon, three intense narrow lines are observed (794, 908, and 1006 cm^{-1}); these stand out quite sharply amongst the other lines of the spectrum.

On analogy with naphthenes, for which the presence of 3-4 sharp intense lines in this frequency region is characteristic – e.g. in the spectra of 1,1-dimethylcyclohexane (706, 828, and 1028 cm^{-1}) and ethylcyclohexane (754, 795, and 1034 cm^{-1}) – we consider that these frequencies are characteristic of a six-membered ring containing a silicon atom.

Turning to the spectrum of the mixture under investigation, we first note the presence of three intense sharp lines coinciding in position with the frequencies noted for the six-membered ring containing silicon, i.e. 800, 909, and 1007 cm^{-1}, their relative intensities being the same as for the silane (II). Similarly, in the region of C–H vibrations we have a group of five lines, 2846, 2872, 2906, 2930, and 2960 cm^{-1}, of which 2906 cm^{-1} is the most intense, 2846 and 2960 cm^{-1} are also intense, and 2872 and 2930 cm^{-1} are the least intense, the character of the distribution of intensities being the same as for the silane (II). This gives us grounds to assert the existence in the mixture of the group

Also, the spectrum contains frequencies of the pentyl group, 1070, 1100, 1187, and about 1451 cm^{-1} (the last line broad) and frequencies of the methyl group, 686, 846, 1256, and 1406 (broad) (the frequencies of 2900 and 2960 cm^{-1} are discussed above). These facts again allow us to consider that the mixture contains a compound with the grouping:



The results of spectrum analysis therefore confirm the results of the physicochemical investigation.

EXPERIMENTAL

Sulfuric acid of density 1.830 was used in all experiments.

Bistetramethylenesilane (I). This was prepared from 60.5 g of 1,4-dibromobutane, 9.0 g of lithium, and 35.8 g of dichloro(tetramethylene)silane in accordance with West's method [3]. The spiran was purified by distillation over sodium and chromatography on silica gel. The yield was 26.6%. The product had b.p. 173-174° (750 mm); n_D^{20} 1.4863; d_4^{20} 0.9043; m.p. –52°; Found MR 44.56; Calculated for C_8SiH_{16} MR 44.54. The literature [3] gives b.p. 178.5° (760 mm); n_D^{25} 1.4860; d_4^{25} 0.899; m.p. < –70°.

Reaction of bistetramethylenesilane (I) with sulfuric acid. A mixture of 4.3 g (0.03 mole) of the spiran (I) and 11.7 g (0.12 mole) of sulfuric acid was shaken for six hours at room temperature. The mixture was treated with water, and the upper layer was separated, washed with sodium carbonate solution, and dried with calcium

chloride. The product, amounting to 4.0 g (90%), was dibutylbistetramethylenedisiloxane (III), b.p. 293.5-294.0° (751 mm); n_D^{20} 1.4670; d_4^{20} 0.9125; found M (cryoscopically in benzene) 288.2; 295.3. Calculated M 298.55. Found MR 90.78; Calculated for $C_{16}Si_2H_{34}O$, MR 90.96.

Found %: C 64.19; 64.07; H 11.64; 11.54; Si 18.84; 18.41. $C_{16}Si_2H_{34}O$. Calculated %: C 64.36; H 11.48; Si 18.80.

Reaction of diethylbistetramethylenedisiloxane (IV) with sulfuric acid. A mixture of 2.8 g (0.011 mole) of the disiloxane (IV) (prepared by method in [6]; b.p. 140.5-141.0° (34 mm); n_D^{20} 1.4641; d_4^{20} 0.9280) and 25.5 g (0.25 mole) of sulfuric acid was shaken for ten hours at room temperature. The mixture was diluted with water, and the upper layer was separated and again shaken with 16.5 g of sulfuric acid for ten hours. The mixture was diluted with water, and the upper layer was washed with sodium carbonate solution and dried with calcium chloride. The product, amounting to 1.8 g (60%) was tetrabutyltetraethylcyclotetrasiloxane (V), b.p. 194-196° (10 mm); n_D^{20} 1.4422; d_4^{20} 0.9286; Found M (cryoscopically in benzene) 506.4; 528.3; Calculated M 520.93; Found MR 148.50; Calculated for $C_{24}Si_4H_{52}O_4$ MR 148.64.

Found %: C 55.53; 55.27; H 10.79; Si 20.99; 21.29. $C_{24}Si_4H_{52}O_4$. Calculated %: 55.33; H 10.83; Si 21.54.

Dimethylpentamethylenesilane (II). A solution of 161 g (0.7 mole) of 1,5-dibromopentane in 500 ml of ether was added to 37 g (1.5 g-atom) of magnesium in 150 ml of ether. The mixture was boiled for two hours; it was then cooled to 5° and a solution of 90 g (0.7 mole) of dichlorodimethylsilane in 1 liter of ether was added in one portion. The mixture was boiled for 15 hours, and the precipitate was then decomposed with water. The ether layer was separated, and the aqueous layer was extracted with two portions of ether. The combined ether solutions were dried with calcium chloride. Ether was distilled off, and the residue then came over at 125-136°. After being distilled over sodium through a 25-plate column and being subjected to chromatography on silica gel, the dimethylpentamethylenesilane had the following properties: b.p. 131.2-131.3° (740 mm); n_D^{20} 1.4428; d_4^{20} 0.8111; Found MR 41.92; Calculated for C_7SiH_{16}, MR 42.04 Calc. 23.9 g (26.7% theory.).

The literature gives: b.p. 133-134° (752.9 mm); n_D^{20} 1.43940; d_4^{20} 0.8039[7] and b.p. 133°, n_D^{25} 1.4380; d_4^{25} 0.798 [3].

Symmetrical tetramethyldipentyldisiloxane (VI). Chlorodimethylpentylsilane (b.p. 166-168°) was prepared in 50% yield from 1.0 mole of dichlorodimethylsilane and 1.0 mole of n-$C_5H_{11}MgBr$ by the Grignard-Wurtz reaction. When 20 g (0.12 mole) of the product was shaken, first with 50 ml of water for ten minutes and then with dilute sulfuric acid, 13 g (77%) of tetramethyldipentyldisiloxane was obtained; b.p. 249.0-249.5° (758 mm); n_D^{20} 1.4226; d_4^{20} 0.8128; Found MR 85.94; Calculated for $C_{14}Si_2H_{34}O$, MR 85.96.

Found %: C 60.96; 61.02; H 12.69; 12.51; Si 20.58; 20.41. $C_{14}Si_2H_{34}O$. Calculated %: C 61.25; H 12.48; Si 20.44.

Reaction of dimethylpentamethylenesilane (II) with sulfuric acid. A mixture of 4.7 g (0.036 mole) of the silane (II) and 10.0 g (0.094 mole) of sulfuric acid was shaken for 13.5 hours at room temperature. There was evolution of gas (425 ml at 0° and 760 mm), and this was found by analysis to be pure methane. The viscous solution formed was treated with water, and the upper layer was washed with sodium carbonate solution and dried with calcium chloride. The experiment was repeated three times, and altogether 12.0 g (85%) of a mixture of disiloxanes was obtained; it had b.p. 245-252°; n_D^{20} 1.4430; d_4^{20} 0.8681; M (cryoscopically in benzene) 257.0, 249.5; Found MR 78.95; Calculated for $C_{14}Si_2H_{34}O$, MR 85.96; for $C_{12}Si_2H_{30}O$ – 73.87; for $C_{15}Si_2H_{32}O$ – 79.20; Calculated M 274.53, 242.18, 258.49 respectively.

Found %: C 60.11; 60.05 H 11.43; 11.65; Si 21.68; 21.52.

$C_{14}Si_2H_{34}O$ (VI). Calculated %: C 61.25; H 12.48; Si 20.44
$C_{12}Si_2H_{30}O$ (VII). Calculated %: C 59.47; H 10.82; Si 23.17
$C_{15}Si_2H_{32}O$ (VIII). Calculated %: C 60.39; H 11.69; Si 21.71

For dimethylbispentamethylenedisiloxane (VI) the literature [3] gives: b.p. 253°; n_D^{25} 1.4640; d_4^{25} 0.927.

Raman spectra (cm^{-1}); the intensities (in parentheses) are estimated visually. For dimethylpentamethylenesilane and bistetramethylenesilane the intensities are given on a scale such that the intensity of the 802 cm^{-1} line of cyclohexane is 250 units.

Bistetramethylenesilane (I) $\Delta\nu$: 242(15), 305(60), 591(25), 618(55), 668(15), 726(10), 757(5), 782(5), 854(60), 946(30), 1026(35), 1068(12), 1156(20), 1200(7), 1254(25), 1340(5), 1414(25), 1457(35), 2854(120), 2870(35), 2895(135), 2945(275).

Dimethylpentamethylenesilane (II) $\Delta\nu$: 105(15 background), 146(30), 203(70), 238(18), 253(15), 334(25 sh), 371(10), 482(10), 585(200), 632(5), 663(2), 694(15), 724(15), 741(5), 794(40 sh), 833(3 b), 908(30), 950(3), 990(8), 1006(40 sh), 1037(2), 1080(12), 1098(10), 1134(15 b), 1180(18), 1193(15), 1251(15), 1268(12), 1291(15), 1333(7), 1408(25), 1445(25), 1460(10), 2846(75), 2874(20), 2900(125 b), 2928(15), 2965(50).

Symm. tetramethyldipentyldisiloxane (VI) $\Delta\nu$: 170(2b), 200(4 b), 479(1), 540(6 b), 652(5), 682(5), 705(3), 763(1), 767(1), 838(0), 895(4), 922(1), 956(4), 1026(3), 1070(3 b), 1102(43a), 1135(4 b), 1186(6 b), 1245(4), 1262 (1), 1304(6), 1336(1), 1380(1), 1410(5), 1443(7), 1456(5), 2858(5 b), 2882(5 b), 2904(10), 2965(10 sh).

Mixture of (VI), (VII), and (VIII) $\Delta\nu$: 184(4 b), 204(4 b), 378(5), 481(1), 520(3), 556(6 b), 658(4 b), 686(2), 717(4 b), 750(1), 767(0), 800(6 sh), 846(0), 878(2), 896(2), 909(6 sh), 956(2), 1007(6 sh), 1042(3), 1070 (4 b), 1100(4 b), 1135(3 b), 1187(4), 1204(4), 1256(4), 1275(1), 1304(5 b), 1336(3 b), 1406(6 b), 1451(6 b), 2846 (10), 2872(5), 2906(10 b), 2930(5), 2960(7).

SUMMARY

1. Bistetramethylenesilane, dimethylpentamethylenesilane, and symmetrical tetramethyldipentyldisiloxane were synthesized.

2. It was shown that silacyclopentanes and their derivatives undergo quantitative scission at the Si–C bond in the ring when treated with concentrated sulfuric acid, the examples taken being bistetramethylenesilane and diethylbistetramethylenedisiloxane.

3. It was shown that, when silacyclohexanes (the example taken being dimethylpentamethylenesilane) react with concentrated sulfuric acid, reaction proceeds in two directions: scission of the Si–C bond in the ring and elimination of a methyl group from the silicon atom.

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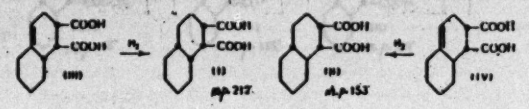
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 13. SYNTHESIS AND STEREOCHEMISTRY OF ISOMERIC DECAHYDRO-1,2-NAPHTHALENEDICARBOXYLIC ACIDS

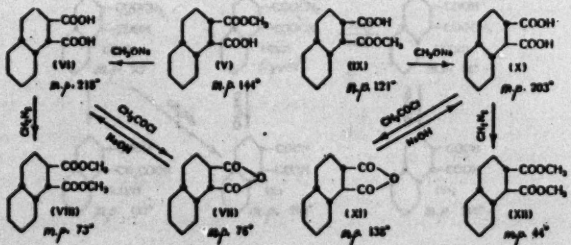
I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

As we showed in a previous communication [1], the hydrogenation of the isomeric adducts (III) and (IV) formed by 1-vinyl-1-cyclohexene with maleic anhydride proceeds in a sterically selective manner with addition of hydrogen at the double bond from the less screened side (opposite to the carboxyls), so that it is possible to obtain the isomeric cis-syn-cis- and trans-anti-cis-decahydro-1,2-naphthalenedicarboxylic acids (I) and (II) quite readily in almost quantitative yield:



The steric nonequivalence of the carboxyls in the isomeric 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (III) and (IV) made it possible for us to prepare the corresponding four isomeric monoesters [2], the hydrogenation of which also proceeds in a sterically selective manner from the side opposite to the carboxyls with formation of four isomeric saturated monoesters (V), (IX), (XIII), and (XVII). These monoesters served us as starting materials for the preparation of new stereoisomers of decahydro-1,2-naphthalenedicarboxylic acid.

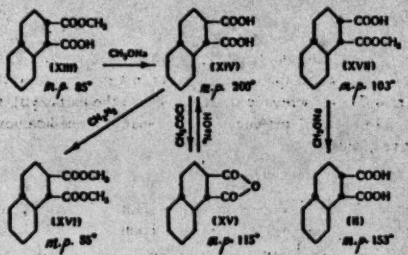
For this purpose we used the reaction of isomerization of the monoesters with sodium methoxide, which, as is well known, occurs at the esterified carboxyl and gives dicarboxylic acids with a trans arrangement of carboxyl groups.



It was found that the cis-syn-cis monoester (V) with an esterified carboxyl at C-2 is very readily isomerized with sodium methoxide with almost quantitative formation of cis-syn-trans-decahydro-1,2-naphthalenedicarboxylic acid (VI), which readily gives the corresponding cis-syn-trans anhydride (VII) and the crystalline cis-syn-trans diester (VIII).

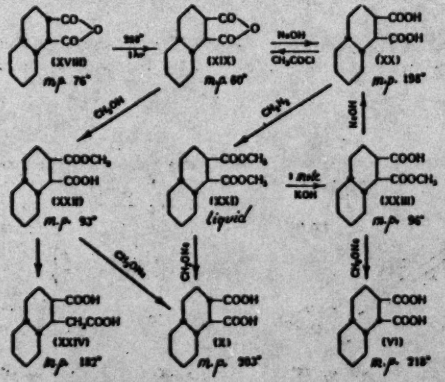
By analogous isomerization at the 1-carboxyl, the isomeric cis-syn-cis monoester (IX) is converted quantitatively into cis-anti-trans-decahydro-1,2-naphthalenedicarboxylic acid (X), which gives the cis-anti-trans anhydride (XI) and the cis-anti-trans diester (XII). The cis-anti-trans acid (X) is readily obtained also by the isomerization of the cis-syn-cis diester (XXVII).

The isomeric monoesters of the trans-anti-cis series (XIII) and (XVII) were also subjected to isomerization with sodium methoxide. It was found, however, that only the trans-anti-cis monoester (XIII), which is esterified at the 2-carboxyl, is isomerized under these conditions, and this gives a good yield of trans-anti-trans decahydro-1,2-naphthalenedicarboxylic acid (XIV), which gives the trans anhydride (XV) and the trans diester (XVI).



The isomeric trans-anti-cis monoester (XVII), which is esterified at the 1-carboxyl, was found to be incapable of undergoing isomerization with sodium methoxide; under such conditions it was quantitatively hydrolyzed into the original trans-anti-cis acid (II).

Yet another stereoisomer of decahydro-1,2-naphthalenedicarboxylic acid was obtained in a study of the thermal isomerization of the cis-syn-cis anhydride (XVIII).

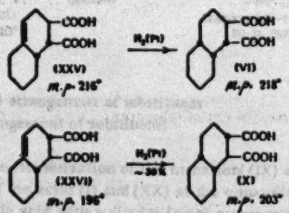


It was found that this anhydride, like the previously studied anhydride of the unsaturated acid (III) [1], is able to undergo thermal isomerization into the more stable cis-anti-cis anhydride (XIX). Similar thermal isomerizations have been described previously for a series of anhydrides of monocyclic o-dicarboxylic acids [3]. Hydrolysis of the cis-anti-cis anhydride (XIX) readily gives cis-anti-cis-decahydro-1,2-naphthalenedicarboxylic acid (XX), from which we prepared the corresponding diester (XXI). The spatial configuration of the cis-anti-cis acid (XX) was proved by studying the isomerization of the corresponding isomeric monoesters (XXII) and (XXIII) in presence of sodium methoxide. These monoesters were prepared by a method described previously [4] – addition of methanol to the cis-anti-cis anhydride (XIX) and partial hydrolysis of the cis-anti-cis diester (XXI).

It was found that, as in the case of the unsaturated acids (III) and (IV) [2], these reactions proceed in a sterically selective manner, and by the action of methanol on the anhydride (XIX) the cis-anti-cis monoester (XXII) with its esterified carboxyl at C-2 was formed, whereas partial hydrolysis of the diester (XXI) gave mainly the isomeric cis-anti-cis monoester (XXIII) with its esterified carboxyl at C-1. The structure of the monoester (XXII) was proved by lengthening of the carbon chain in an Arndt-Eistert reaction and dehydrogenation of the 2-carboxydecahydro-1-naphthaleneacetic acid (XXIV) obtained to 1-methylnaphthalene. The structure of the isomeric monoester (XXIII) was proved by the fact that it was converted by hydrolysis into the original cis-anti-cis acid (XX).

When the monoester (XXII) was boiled with sodium methoxide, isomerization at the esterified 2-carboxyl occurred with formation of the cis-anti-trans acid (X), already obtained from the cis-syn-cis monoester (IX). The same acid (X) is readily prepared also by the isomerization of the diester (XXI). On the other hand, the monoester (XXIII) with an esterified 1-carboxyl reacts under these conditions with formation of the cis-syn-trans acid (VI), identical with the acid obtained previously by the isomerization of the cis-syn-cis monoester (V). It is not difficult to see that such transformations can occur only if the acid (XX) has a cis-anti-cis configuration.

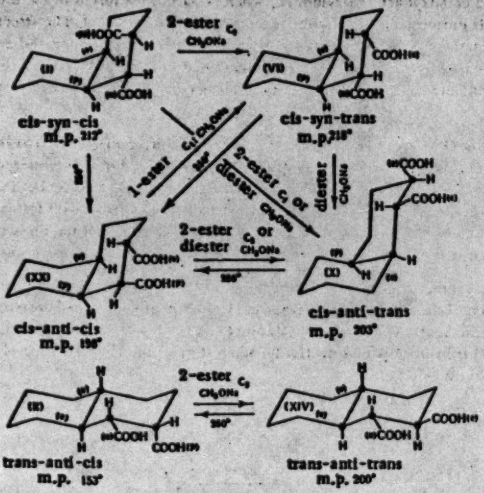
With the object of synthesizing other possible isomers of decahydro-1,2-naphthalenedicarboxylic acid, we studied the hydrogenation of the previously described [2] isomeric syn-trans- and anti-trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids (XXV) and (XXVI). It was found, however, that of these acids only the syn-trans acid (XXV) is hydrogenated selectively, when it gives the above-described cis-syn-trans-decahydro-1,2-naphthalenedicarboxylic acid (VI).



The anti-trans acid (XXVI) is hydrogenated to a mixture of saturated acids, and by fractional crystallization of this mixture was isolated only a small amount of the cis-anti-trans acid (X). These results are strictly in accordance with molecular models [2], from which it follows that in the acid (XXV) the carboxyls have a screening effect, whereas in the acid (XXVI) such screening is absent.

We have thus prepared six out of the eight theoretically possible isomers of decahydro-1,2-naphthalenedicarboxylic acid, four of these, (I), (VI), (X), and (XX), belonging to the cis-decahydronaphthalene series, and the other two, (II) and (XIV), to the trans-decahydronaphthalene series. The preparation of these isomers by stereospecific mutual transformations leaves no doubt about the correctness of the configurations attributed to them. Moreover, the steric structures of trans-anti-cis- and trans-anti-trans-decahydro-1,2-naphthalenedicarboxylic acids (II) and (XIV) were recently rigorously proved by special synthesis via decahydro-4-oxo-1,2-naphthalenedicarboxylic acid [5].

An examination of molecular models of isomeric decahydro-1,2-naphthalenedicarboxylic acids confirms our conclusions regarding their spatial configurations derived from a study of the thermal transformations of these acids and the isomerization of the corresponding esters in presence of sodium methoxide. As the models show, the isomerization of the cis-syn-cis acid (I) [in the form of its monoester(V)] with sodium methoxide at the polar 2-carboxyl and the analogous isomerization of the cis-anti-cis acid (XX)[in the form of its monoester (XXIII)] at the polar 1-carboxyl will readily give the same cis-syn-trans acid (VI) with a diequatorial (trans) arrangement of carboxyls. In a similar way, the trans-anti-cis acid (II) [in the form of its monoester (XIII)] is readily isomerized at its polar 2-carboxyl into the trans-anti-trans acid (XIV), which also has a diequatorial (trans) arrangement of carboxyls.



(e) – equatorial arrangement of substituent
(p) – polar arrangement of substituent

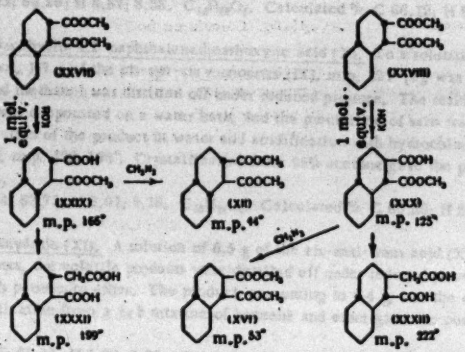
Different behavior is found in the isomerization of the monesters (IX) and (XXII) with sodium methoxide [corresponding to the transformation of the acids (I) and (XX) at the equatorial 1- and 2-carboxyls]. In this case isomerization should lead to an unstable acid with a dipolar (p – p) arrangement of carboxyl groups, and, owing to the mobility of the cis-decahydronaphthalene system, this acid will undergo spontaneous rearrangement into the stable cis-anti-trans acid (X) with a diequatorial (trans) arrangement of carboxyls. A similar rearrangement of rings occurs also in the case of the diesters (XXVII) and (XXI) [corresponding to the acids (I) and (XX)], which in isomerization with sodium methoxide are converted not into the cis-syn-trans acid (VI), but into the stable cis-anti-trans acid (X).

Hence, the isomerization of the diesters (XXVII) and (XXI) appears to occur at equatorial carboxyls with subsequent rearrangement of the rings with formation of the more stable cis-anti-trans configuration.

In a similar way, under the conditions of isomerization with sodium methoxide, the trans diester (XIII), which corresponds to the cis-syn-trans acid (VI), is partially converted into the cis-anti-trans acid (X). In the stable trans-decahydronaphthalene series such a rearrangement of rings cannot occur, so that isomerization of the trans-anti-cis acid (II) at the 1-carboxyl does not occur and the monoester (XVII) is merely hydrolyzed to the original acid (II) under these conditions.

Study of thermal transformations showed that, of the four acids of the cis-decahydronaphthalene series, the most stable thermally is the cis-anti-cis acid (XX), the anhydride of which (XIX) is the product obtained when the other three acids of the cis-decahydronaphthalene series (I), (VI), and (X) are heated at 250°. Similarly, the trans-anti-trans acid (XIV) is readily isomerized at 250° into the anhydride of the trans-anti-cis acid (II). All these data on the mutual transformations of the six isomeric decahydro-1,2-naphthalenedicarboxylic acids that we have prepared are in full accord with previously established facts concerning the higher stability of the anti configuration at the 1–8a bond [6] and the higher thermal stability of the cis configuration of a five-membered anhydride ring [7].

Some supplementary data on the stereochemistry of isomeric acids of the cis-decahydronaphthalene series were obtained in a study of the partial hydrolysis of the isomeric diesters (XXVII) and (XXVIII). It was found that both of these esters are isomerized to a considerable extent when hydrolyzed with one molecular equivalent of potassium hydroxide, the products being the crystalline monoesters (XXIX) and (XXX) with a trans arrangement of carboxyls; the spatial configurations of these products were proved by their conversion into the above-described diesters (XII) and (XVI) with the aid of sodium methoxide.



When subjected to Arndt-Eistert chain lengthening, the monesters (XXIX) and (XXX) gave the isomeric 1-carboxydecahydro-2-naphthaleneacetic acids (XXXI) and (XXXII), dehydrogenation of which gave 2-methylnaphthalene. This proved that both trans monoesters (XXIX) and (XXX) have the esterified group at C-1, so that even under mild conditions (1 molecular equivalent of potassium hydroxide) the cis-syn-cis diester (XXVII) is readily isomerized and, owing to rearrangement of the bicyclic system, gives a cis-anti-trans configuration with a diequatorial (e–e) arrangement of carboxyls. On the other hand, in hydrolysis with one molecular equivalent of potassium hydroxide, the trans-anti-cis diester (XXVIII) undergoes only isomerization at the polar 2-carboxyl.

EXPERIMENTAL

cis-syn-trans-Decahydro-1,2-naphthalenedicarboxylic acid (VI). To a solution of 5 g of sodium in 120 ml of absolute methanol, 2 g of the cis-syn-cis monoester (V), m.p. 144° [2], was added, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure and the residue was dissolved in 100 ml of water. The solution was filtered and was evaporated on a water bath to a thick slurry. The precipitate of salts was filtered off, washed with absolute methanol, and dissolved in 50 ml of water. Acidification of the filtered solution with hydrochloric acid gave 1.75 g of the cis-syn-trans acid (VI), m.p. 213-215°, raised to a constant value of 217-218° (with decomposition) by crystallization from acetone.

Found %: C 63.85; 63.64; H 7.99; 8.91. $C_{12}H_{18}O_4$. Calculated %: C 63.68; H 8.02.

The diphenacyl ester, prepared in the usual way, melted at 98-99° after recrystallization from alcohol.

Found %: C 72.61; 72.92; H 6.56, 6.55. $C_{22}H_{30}O_6$. Calculated %: C 72.71; H 6.54.

cis-syn-trans Anhydride (VII). A solution of 0.5 g of the cis-syn-trans acid (VI) in 5 ml of acetyl chloride was boiled for one hour, and the volatile products were distilled off under reduced pressure. The liquid residue was evaporated with benzene under reduced pressure, treated with petroleum ether, and left overnight at 0°. The crystalline product was washed on the filter with petroleum ether, and 0.4 g of the anhydride (VII), m.p. 70-73°, was obtained. After two recrystallizations from petroleum ether, the anhydride (VII) had a constant melting point of 75-76°.

Found %: C 68.97; 69.17; H 7.67; 7.56. $C_{22}H_{26}O_3$. Calculated %: C 69.21; H 7.74.

Hydrolysis of the cis-syn-trans anhydride (VII) with aqueous sodium hydroxide (5%) at the boil gave pure original cis-syn-trans acid (VI), m.p. 215-216°.

cis-syn-trans Diester (VIII). The cis-syn-trans acid (VI) (0.7 g) was treated with ethereal diazomethane, ether was distilled off, and the residue was washed with petroleum ether. A yield of 0.65 g of (VIII), m.p. 63-65°, was obtained; after crystallization from petroleum ether it melted at 72-73°.

Found %: C 66.23; 66.20; H 8.67; 8.55. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

cis-anti-trans-Decahydro-1,2-naphthalenedicarboxylic acid (X). To a solution of 4.2 g of sodium in 100 ml of absolute methanol, 1.7 g of the cis-syn-cis monoester (IX), m.p. 121° [2], was added, the mixture was boiled for 16 hours, and methanol was distilled off under reduced pressure. The residue was dissolved in 30 ml of water, the solution was evaporated on a water bath, and the precipitate of salts was filtered off and washed with methanol. Dissolution of the product in water and acidification with hydrochloric acid gave 1.6 g of the cis-anti-trans acid (X), m.p. 196-198°. Crystallization from 25% acetone gave the pure acid, m.p. 202-203°.

Found %: C 63.74; 63.75; H 8.01; 8.18. $C_{12}H_{18}O_4$. Calculated %: C 63.68; H 8.02.

cis-anti-trans Anhydride (XI). A solution of 0.5 g of the cis-anti-trans acid (X) in 5 ml of acetyl chloride was boiled for 40 minutes, the volatile products were distilled off under reduced pressure, and the residue crystallized when treated with petroleum ether. The product, amounting to 0.4 g, was the cis-anti-trans anhydride (XI), m.p. 135-137°; crystallization from a 1:2 mixture of benzene and ether gave the pure anhydride, m.p. 137-138°.

Found %: C 69.07; 69.17; H 7.57; 7.70. $C_{12}H_{16}O_3$. Calculated %: C 69.21; H 7.74.

Hydrolysis with 5% sodium hydroxide solution gave a quantitative yield of the original cis-anti-trans acid (X), m.p. 201-202°.

cis-anti-trans Diester (XII). A suspension of 1.5 g of the cis-anti-trans acid (X) in ether was treated with ethereal diazomethane, ether was distilled off, and the crystalline residue was washed on the filter with petroleum ether. The product, amounting to 1.3 g, was the cis-anti-trans diester (XII), m.p. 39-42°, raised to 43-44° by crystallization from petroleum ether.

Found %: C 65.97; 65.72; H 8.70; 8.74. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

trans-anti-trans-Decahydro-1,2-naphthalenedicarboxylic acid (XIV). To a solution of 6.5 g of sodium in 220 ml of absolute methanol, 2.7 g of the trans-anti-cis monoester (XIII), m.p. 85° [2], was added, the mixture was boiled for 17 hours, methanol was distilled off under reduced pressure, and the residue was dissolved in 60 ml of water. The solution was filtered and evaporated in a porcelain dish on a water bath. The precipitate of salts was filtered off, washed with methanol, and dissolved in 15 ml of water. Acidification of the solution with hydrochloric acid gave 2.4 g of the trans-anti-trans acid (XIV), m.p. 194-196°, raised to 199-200° by crystallization from 25% acetone; it gave a marked depression of melting point (to 175-190°) in admixture with the acid (X).

Found %: C 63.69; 63.58; H 7.98; 7.92. $C_{12}H_{18}O_4$. Calculated %: C 63.68; H 8.02.

trans-anti-trans anhydride (XV). Boiling with acetyl chloride in the usual way converted 0.5 g of the trans-anti-trans acid (XIV) into 0.43 g of the trans-anti-trans anhydride (XV), m.p. 113-115°; after crystallization from a mixture of diethyl ether and petroleum ether it melted at 114-115°.

Found %: C 68.98; 69.20; H 7.75; 7.54. $C_{12}H_{16}O_3$. Calculated %: C 69.21; H 7.74.

Hydrolysis of (XV) with boiling 5% sodium hydroxide converted it quantitatively into the original trans-anti-trans acid (XIV), m.p. 198-199°.

trans-anti-trans Diester (XVI). One g trans-anti-trans acid (XIV) was treated with ethereal diazomethane giving 1 g trans-anti-trans diester (XVI), m.p. 49-51°, which after crystallization from petroleum ether had constant m.p. 54-55°.

Found%: C 66.14; 66.31; H 8.65; 8.75. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

Attempt to isomerize the trans-anti-cis monoester (XVII). To a solution of 6.5 g of sodium in 220 ml of absolute methanol, 2.7 g of the trans-anti-cis monoester (XVII), m.p. 103° [2], was added, and the mixture was boiled for 17 hours. The usual treatment gave 2.4 g of the trans-anti-cis acid (II), m.p. 147-148°, raised to 151-153° by crystallization from 25% acetone. There was no depression of melting point in admixture with the previously described sample [2].

cis-anti-cis Anhydride (XIX). The cis-syn-cis anhydride (XVIII) (17.4 g), m.p. 76° [2], was heated for one hour in a stream of nitrogen at 245-255° and then for a further ten minutes at 275°. Vacuum distillation of the product gave 13.2 g of the cis-anti-cis anhydride (XIX) in the form of a thick oil, b.p. 195-196° (14 mm). It gradually crystallized to a solid of m.p. 46-50°, raised to 59-60° by crystallization from a 1 : 5 mixture of diethyl ether and petroleum ether.

Found %: C 69.04; 69.16; H 7.57; 7.70. $C_{12}H_{16}O_3$. Calculated %: C 69.21; H 7.74.

cis-anti-cis-Decahydro-1,2-naphthalenedicarboxylic acid (XX). A mixture of 7.1 g of the cis-anti-cis anhydride (XIX) and 80 ml of 5% sodium hydroxide solution was boiled for ten minutes. Acidification with hydrochloric acid gave 7.5 g of the cis-anti-cis acid (XX), m.p. 187-190°, raised to 197-198° by crystallization from 70% acetone.

Found %: C 63.85; 63.98; H 8.34; 8.24. $C_{12}H_{18}O_4$. Calculated %: C 63.68; H 8.02.

cis-anti-cis Diester (XXI). The cis-anti-cis acid (XX) (4.5 g) was treated with a preparation of ethereal diazomethane, ether was distilled off, and the liquid residue was vacuum-distilled. The product, amounting to 4.6 g, was the cis-anti-cis diester (XXI), b.p. 131-132° (2 mm); n_D^{20} 1.4874; d_4^{20} 1.1241; MR 65.11, Calc. MR 65.48

Found %: C 66.06; 66.04; H 8.70; 8.86. $C_{14}H_{22}O_4$. Calculated %: C 66.12; H 8.72.

cis-anti-cis Monoester (XXII). A mixture of 5.5 g of the cis-anti-cis anhydride (XIX) and 25 ml of absolute methanol was boiled for one hour, methanol was distilled off under reduced pressure, and the crystalline residue was washed on the filter with petroleum ether. The product, amounting to 4.8 g was the cis-anti-cis monoester (XXII), m.p. 86-89°, raised to 92-93° by crystallization from a 1 : 3 mixture of diethyl ether and petroleum ether.

Found %: C 64.85; 65.04; H 8.28; 8.39. $C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

When subjected to isomerization with sodium methoxide according to the above-described procedure, 2.1 g of the cis-anti-cis monoester (XXII) gave 1.9 g of an acid of m.p. 193-195°, raised to 200-202° by crystallization from 25% acetone; it showed no depression of melting point in admixture with a pure sample of the cis-anti-trans acid (X).

cis-anti-cis Monoester (XXIII). The cis-anti-cis diester (XXI) (4.6 g) was added to a solution of 0.99 g of potassium hydroxide in 16 ml of water and 50 ml of methanol, and the mixture was boiled for two hours. Methanol was distilled off under reduced pressure, and the aqueous solution was extracted with ether and acidified with hydrochloric acid. The oil that separated was extracted with ether, the ether extract was dried with sodium sulfate, and the ether was distilled off. The liquid product was dissolved in 15 ml of petroleum ether, a small amount of heterogeneous high-melting substance was filtered off, and the solution was evaporated to small bulk and left at 0° overnight. The crystals that separated were filtered off and washed with cold petroleum ether. The product, amounting to 2.2 g, was the cis-anti-cis monoester (XXIII), m.p. 88-91°, raised to a constant value

of 95-96° by crystallization from a mixture of diethyl ether and petroleum ether. A mixture with the isomeric cis-anti-cis monoester (XXII) melted at 65-75°.

Found %: C 64.90; 64.96; H 8.19; 8.45. $C_{13}H_{20}O_4$. Calculated %: C 65.01; H 8.33.

When subjected to isomerization with sodium methoxide according to the above-described procedure, 1 g of the cis-anti-cis monoester (XXIII) gave 0.88 g of the cis-syn-trans acid (VI), m.p. 210-212°, raised to 217-218° by crystallization from acetone; it gave no melting point depression with sample prepared previously.

cis-anti-cis-2-Carboxydecahydro-1-naphthaleneacetic acid (XXIV). A mixture of 3 g of cis-anti-cis monoester (XXII), 20 ml of dry benzene, and 1 ml of oxalyl chloride was heated at 60° for two hours. Benzene was distilled off under reduced pressure, and the liquid acid chloride was dissolved in 15 ml of dry ether. The solution was added with cooling and stirring to a solution of 4 g of diazomethane in 200 ml of dry ether and left overnight. Ether was distilled off, and the residue was dissolved in 60 ml of absolute methanol. Freshly prepared silver oxide (1 g) was added, and the mixture was boiled for five hours. The precipitate was filtered off, methanol was distilled off, and the liquid residue was vacuum-distilled. The product, amounting to 2.4 g, was the dimethyl ester of 2-carboxydecahydro-1-naphthaleneacetic acid (XXIV), b.p. 156° (4 mm) and on n_D^{20} 1.4860.

Found %: C 67.23; 67.37; H 8.86; 8.77. $C_{15}H_{24}O_4$. Calculated %: C 67.16; H 9.01.

In order to hydrolyze the ester of (XXIV), 2.2 g was boiled with 12 ml of 20% potassium hydroxide solution for four hours. Acidification with hydrochloric acid gave 1.7 g of the acid, m.p. 145-160°. Two crystallizations from 50% aqueous acetone gave 1.1 g of cis-anti-cis-2-carboxydecahydro-1-naphthaleneacetic acid (XXIV) having a constant melting point of 180-182°.

Found %: C 65.00; 65.09; H 8.32; 8.33. $C_{13}H_{21}O_4$. Calculated %: C 65.01; H 8.33.

In order to dehydrogenate the acid (XXIV), 1.05 g was heated as a solution in 20 ml of benzene with 0.5 g of palladized charcoal (10% Pd) for 16 hours at 360-370°. Distillation gave 0.4 g of dehydrogenation product, b.p. 210-232°, n_D^{20} 1.5574. The product formed a picrate of m.p. 137-138°, undepressed by admixture of pure 1-methylnaphthalene picrate (138-140°).

Hydrogenation of syn-trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid (XXV). In the hydrogenation of 2.2 g of the syn-trans acid (XXV) as a solution in 20 ml of absolute methanol in presence of platinum oxide, one molecular equivalent (230 ml at 0° and 760 mm) of hydrogen was absorbed. Methanol was distilled off under reduced pressure, and the crystalline product was washed on the filter with a little 50% aqueous acetone. The product, amounting to 2.1 g, was pure cis-syn-trans acid (VI), m.p. 216-217°, undepressed by admixture of the sample described above.

Hydrogenation of anti-trans-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid (XXVI). In the hydrogenation of 2.5 g of the anti-trans acid (XXVI) as a solution in 25 ml of methanol in presence of platinum oxide, one molecular equivalent (260 ml) of hydrogen was absorbed. After removal of methanol there remained a liquid product which solidified when treated with water (2.2 g, m.p. 170-185°). As a result of two fractional crystallizations of this mixture from 40% aqueous acetone, 0.9 g of the cis-anti-trans acid (X) was isolated; it had m.p. 200-202°, undepressed by admixture of the above-described sample.

We did not suceed in isolating any other pure substances.

Thermal transformations of isomeric decahydro-1,2-naphthalenedicarboxylic acids. a) The cis-anti-trans acid (X) (0.5 g) was heated in a stream of nitrogen for 45 minutes at 250-255° and then for a further five minutes at 270-275°. Vacuum distillation of the product gave 0.4 g of a viscous liquid having b.p. 185-190° (10 mm) and n_D^{20} 1.5110, which was hydrolyzed at the boil with 5 ml of 5% sodium hydroxide solution. The crystals formed on acidification (0.3 g, m.p. 185-188°) were crystallized from 70% aqueous acetone. They then melted at 196-197° and were found to be identical with the cis-anti-cis acid (XX).

b) In a similar way, 0.9 g of the cis-syn-trans acid (VI) gave 0.6 g of a liquid anhydride, which, after hydrolysis and crystallization of the product from 50% acetone, gave 0.5 g of pure cis-anti-cis acid (XX), m.p. 197-198° and identical with the samples described above.

c) The trans-anti-trans acid (XIV) (0.9 g) was heated in a stream of nitrogen for 45 minutes at 250-255° and the product was vacuum-distilled. The isomerization product solidified when distilled; it was washed with ether. The product, amounting to 0.6 g, was the anhydride of the trans-anti-cis acid (II), m.p. 126-127° and identical with the substance obtained previously [1]. Hydrolysis with aqueous sodium hydroxide gave the pure trans-anti-cis acid (II), m.p. 151-153°, undepressed by admixture of an authentic sample.

cis-anti-trans Monoester (XXIX). The cis-syn-cis diester (XXVII) (11.6 g) was added to a solution of 2.5 g of sodium hydroxide in 125 ml of methanol and 40 ml of water, and the mixture was boiled for two hours. Methanol was distilled off under reduced pressure, and the aqueous solution was extracted with ether and acidified with hydrochloric acid. The crystalline product was filtered off and carefully washed with a 2:1 mixture of ether and acetone. The product, amounting to 4.2 g, was the cis-anti-trans monoester (XXIX), m.p. 160-162°, raised to a constant value of 165-166° by crystallization from acetone.

Found %: C 64.95; 64.79; H 8.34; 8.43. $C_{19}H_{28}O_4$. Calculated %: C 65.01; H 8.33.

When the cis-anti-trans monoester (XXIX) was treated with ethereal diazomethane, the cis-anti-trans diester (XII) of m.p. 43-44° described above was obtained in quantitative yield.

trans-anti-trans Monoester (XXX). By similar partial hydrolysis, 6 g of the trans-anti-cis diester (XXVIII) gave 2.1 g of the trans-anti-trans monoester (XXX), m.p. 120-122°, raised to 124-125° by crystallization from a 1:1 mixture of diethyl ether and petroleum ether.

Found %: C 64.81; 64.76; H 8.26; 8.31. $C_{19}H_{28}O_4$. Calculated %: C 65.01; H 8.33.

Treatment of this monoester with diazomethane gave the trans-anti-trans diester (XVI), m.p. 52-53° and identical with the sample obtained previously.

cis-anti-trans-1-Carboxyldecahydro-2-naphthaleneacetic acid (XXX). A mixture of 3.1 g of the cis-anti-trans monoester (XXIX), 20 ml of dry benzene, and 1 ml of oxalyl chloride was heated at 50° for three hours. Benzene was distilled off under reduced pressure, and the resulting liquid acid chloride was dissolved in 15 ml of dry ether. This solution was added slowly with cooling to a dry solution of 4.5 g of diazomethane in 150 ml of ether, and the solution was left overnight at room temperature. On the next day ether was distilled off and the residue was dissolved in 60 ml of absolute methanol; 1 g of silver oxide was added, and the mixture was boiled for seven hours. Silver oxide was filtered off, methanol was distilled off under reduced pressure, and the residue was vacuum-distilled, yielding 2.9 g of the dimethyl ester of the acid (XXXI), b.p. 145-146° (3 mm) and n_D^{23} 1.4836.

Found %: C 67.15; 66.96; H 9.03; 8.93. $C_{15}H_{24}O_4$. Calculated %: C 67.16; H 9.01.

In order to hydrolyze the ester, 2.6 g was boiled with 14 ml of 20% sodium hydroxide solution for four hours. The oil formed on acidification rapidly solidified, and in this way 2.2 g of an acid of m.p. 175-185° was obtained. Two crystallizations from 50% aqueous acetone gave 1.8 g of the acid (XXXI) having a constant melting point of 198-199°.

Found %: C 64.95; 65.02; H 8.33; 8.32. $C_{13}H_{21}O_4$. Calculated %: C 65.01; H 8.33.

In order to dehydrogenate the acid (XXXI), a mixture of 1.2 g of the acid, 20 ml of benzene, and 0.5 g of palladized charcoal (10% Pd) was heated in a nitrogen atmosphere at 360-370° for 16 hours. Distillation gave 0.55 g of the dehydrogenation product, b.p. 210-235° and n_D^{20} 1.5510. The picrate prepared from this had m.p. 114-115°, undepressed by admixture of a known sample of 2-methylnaphthalene picrate.

trans-anti-trans-1-Carboxydecahydro-2-naphthaleneacetic acid (XXXII). In a similar way, 2 g of the trans-anti-trans monoester (XXX) was submitted to the Arndt-Eistert reaction and gave, after distillation, 1.6 g of the dimethyl ester of the acid (XXXII), b.p. 148-150° (3 mm); n_D^{20} 1.4814.

Found %: C 67.26; 67.28; H 8.05; 9.08. $C_{15}H_{24}O_4$. Calculated %: C 66.12, H 8.72.

Hydrolysis of 1.5 g of this diester by treatment with a solution of 3.5 g of potassium hydroxide in 5 ml of water at the boil gave 1.2 g of the acid (XXXII), m.p. 212-215°, raised to 218-220° by crystallization from 50% acetone.

Found %: C 64.99; 65.11; H 8.43; 8.35. $C_{12}H_{21}O_4$. Calculated %: 65.01; H 8.23.

In order to dehydrogenate the acid (XXXII), 1.1 g was heated as a solution in 20 ml of benzene with 0.5 g of palladized charcoal (360-370°, 18 hours). Distillation gave 0.45 g of dehydrogenation product, b.p. 220-235° and n_D^{20} 1.5554. The picrate of the product had m.p. 115-116°, undepressed by admixture of known 2-methylnaphthalene picrate.

Isomerization of the cis-syn-cis diester (XXVII). The cis-syn-cis diester (XXVII) (4.0 g) was added to a solution of 9.7 g of sodium in 250 ml of absolute methanol, and the mixture was boiled for 18 hours. The above described treatment gave 3.2 g of the cis-anti-trans acid (X), m.p. 190-192°, raised to 202-203° by crystallization from 25% aqueous acetone; there was no depression of melting point in admixture with the sample prepared previously (above).

Isomerization of the cis-anti-cis diester (XXI). In the same way, 0.8 g of the cis-anti-cis diester (XXI) was isomerized with a boiling solution of 1.9 g of sodium in 50 ml of absolute methanol for a period of 17 hours. The product, amounting to 0.6 g, was the cis-anti-trans acid (X), m.p. 189-193°, raised to 202-203° by crystallization from 30% acetone; there was no depression of melting point in admixture with a known sample.

Isomerization of the cis-syn-trans diester (VIII). In the same way, after the isomerization of 1.0 g of the diester (VIII) by boiling it for 16 hours with a solution of 2.5 g of sodium in 60 ml of absolute methanol, 0.75 g of an acid of m.p. 187-190° was obtained. Two crystallizations from 30% aqueous acetone gave 0.25 g of the cis-anti-trans acid (X), m.p. 200-202°, undepressed by admixture of samples prepared previously (above).

SUMMARY

1. Six of the eight theoretically possible isomers of decahydro-1,2-naphthalenedicarboxylic acid (I), (II), (VI), (X), (XIV), and (XX) are described, and in each case a rigorous determination of spatial configuration is made.

2. A study is made of the chemical transformations of all the synthesized isomeric decahydro-1,2-naphthalenedicarboxylic acids and of the cis-trans isomerization of the corresponding mono- and di-esters in presence of sodium methoxide. It is shown that the isomers obtained are relatively stable both to heat and to alkaline reagents.

3. On the basis of the theory of equatorial-polar bonds in the cyclohexane molecule and of an examination of molecular models, all the peculair features of the mutual transofrmations of the six isomeric decahydro-acids and their esters can be explained.

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*T.p = C. B. Translation pagination.

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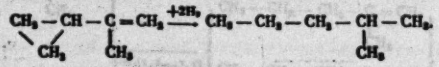
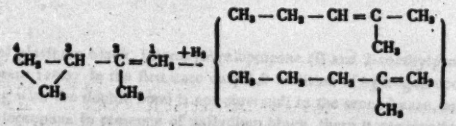
HYDROGENATION OF ISOPROPENYLCYCLOPROPANE IN PRESENCE OF PLATINUM BLACK

B. A. Kazansky, M. Yu. Lukina, A. I. Malyshev, V. T. Aleksanyan, and Kh. E. Sterin

We have observed previously [1] that in the hydrogenation of isopropenylcyclopropane in alcholic solution at room temperature in presence of palladium black addition of two molecules of hydrogen occurs with formation of 2-methylpentane:



A study of this reaction showed that 2-methylpentane is formed by the hydrogenation of the first-formed 2-methyl-1-pentene and 2-methyl-2-pentene. It was suggested that these methylpentenes are formed as a result of 1,3- and 3,4-addition of hydrogen to isopropenylcyclopropane, in which the double bond is conjugated with the three-membered ring:



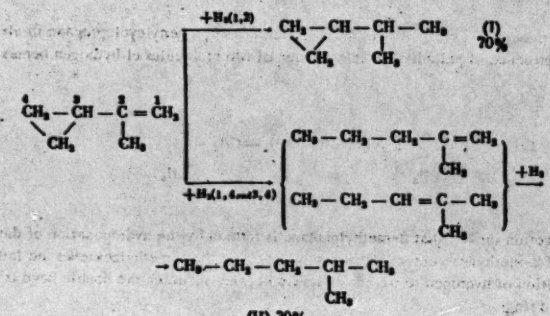
We did not succeed in establishing the positions in which addition of hydrogen occurred (1,4 or 3,4 or both simultaneously), for it was found that in presence of palladium black under the experimental conditions used 2-methyl-1-pentene and 2-methyl-2-pentene are isomerized into one another with formation of an equilibrium mixture. No 1,2-addition of hydrogen occurred; the product of such addition, isopropylcyclopropane, was not detected either as a final product or as an intermediary. Continuing the study of this reaction, we carried it out under the same conditions but with platinum black as catalyst in place of palladium black. We then found that in presence of platinum black the amount of hydrogen absorbed by one molecular proportion of isopropenylcyclopropane was not two molecular proportions, but only 1.3; absorption then ceased, and no further absorption occurred when a new portion of catalyst was added. The bromine water test indicated absence of unsaturated compounds in the catalyzate. Fractionation through a 40-plate column showed that the catalyzate consisted of a mixture of hydrocarbons of similar boiling points, so that we could not separate them by distillation. The physical constants of the product indicated that it was a mixture of isopropylcyclopropane and 2-methylpentane, and a Raman-spectrum study confirmed this view; the catalyzate consisted of 70% of isopropylcyclopropane and 30% of 2-methylpentane.

In order to elucidate the mechanism of the hydrogenation, we carried out a series of experiments in which the addition of hydrogen to isopropenylcyclopropane was discontinued as soon as 0.65 or 1 molecular proportion of hydrogen had been absorbed. Raman-spectrum investigations on the catalyzates showed that, apart from

isopropenylcyclopropane, isopropylcyclopropane, and 2-methylpentane, 2-methyl-1-pentene and 2-methyl-2-pentene were also present.

In order to determine whether isopropenylcyclopropane underwent isomerisation under the conditions of hydrogenation, we carried out experiments in which the addition of hydrogen was stopped as soon as 0.2 of a molecular proportion had been absorbed. Investigation with the aid of Raman spectra showed that the catalyzate consisted mainly of unchanged isopropenylcyclopropane together with some isopropylcyclopropane and traces of 2-methyl-2-pentene.

It was established by special experiments that, in contrast with the behavior found for palladium black, in presence of platinum black 2-methyl-1-pentene and 2-methyl-2-pentene are not isomerized into one another. It was established also that under the given conditions in presence of either catalyst, hydrogen does not add to isopropylcyclopropane, i.e the three-membered ring remains intact. On the basis of all these results we may suppose that the hydrogenation of isopropenylcyclopropane in presence of platinum black proceeds in accordance with the following scheme:



Hence, in presence of platinum black, isopropylcyclopropane (I) and 2-methylpentane (II) are formed simultaneously but at different rates. In the first case only 1,2-addition of hydrogen occurs, and conjugation of of the three-membered ring with the double bond is not observed; in the second case, as in the case of the hydrogenation of isopropenylcyclopropane in presence of palladium black, there is conjugation of the three-membered ring and the double bond and 1,4- and 3,4-addition of hydrogen occurs. When we consider the amounts of hydrogen added in the two reactions, it becomes clear why absorption ceases after the addition of 1.3 of a molecular proportion in presence of platinum.

EXPERIMENTAL

1. Hydrocarbons and Catalysts

Isopropylcyclopropane was prepared by the hydrogenation of isopropenylcyclopropane over a copper chromate catalyst, the product being distilled through a 100-plate column. The purity of the hydrocarbon so obtained was estimated at about 97% on the basis of its refractive index and specific volume: b.p. 58.4° (760 mm); n_D^{20} 1.3859; d_4^{20} 0.6968; aniline point 34.9°. Raman spectrum: *

$\Delta\nu$ (cm^{-1}) 237(2), 260(0), 296(14), 339(17), 440(2), 465(39), 708(12), 737(45), 798(8), 818(16,b), 872(71), 904(18), 922(6), 951(8), 961(2), 991(0), 1014(2), 1041(7), 1065(1), 1096(7), 1123(15), 1135(12), 1161(0), 1174(2), 1193(92), 1209(11), 1219(15), 1284(4), 1311(11), 1331(3), 1372(2), 1387(18), 1427(18), 1453(28,b), 1467(24,b), 2713(30), 2753(5), 2870(130), 2912(65), 2940(30, background), 2959(90), 2990(50,b), 3004(140), 3065(60), 3074(60).

* Laboratory worker V. M. Gorokhova took part in the investigation of the Raman spectra.

Isopropenylcyclopropane, 2-methyl-1-pentene, and 2-methyl-2-pentene were synthesized by the methods described previously [1]. In the same paper the constants and Raman spectra of these compounds were given. The reported constants of isopropenylcyclopropane and the hydrocarbons that can be obtained from it by hydrogenation are given in Table 1.

TABLE 1

Hydrocarbon	B.p. (°C)	n_D^{20}	d_4^{20}
Isopropylcyclopropane [2]	58.37	1.38639	0.69829
Isopropenylcyclopropane [2]	70.33	1.42550	0.75153
2-Methyl-1-pentene [3]	60.7	1.3915	0.6817
2-Methyl-2-pentene [3]	67.29	1.4004	0.6863
3-Methylpentane [3]	60.271	1.37145	0.65315

Platinum Black was prepared by Zelinsky's method [4]. The same batch of catalyst was used in all the experiments.

Palladium Black was prepared from palladous chloride by Zelinsky's method [4].

2. Experimental Procedure

Hydrogenation was carried out in a 100-ml hydrogenation flask of the usual type at 18-20°. In each experiment a fresh 0.4 g portion of catalyst was used, and reaction was with electrolytic hydrogen in 40 ml of distilled ethanol. Catalyst was filtered off, and the hydrogenation product was distilled as an azeotropic mixture with alcohol through a column with a glass packing. It was then washed with water, dried, and fractionated through a 40-plate column with a copper packing. In all these fractionations through a column, 7 ml of heptane (n_D^{20} 1.3877) was added as a displacer.

Isomerization experiments were carried out under the same conditions as the hydrogenation experiments, 20% of the hydrogen theoretically necessary for hydrogenation being added. The catalyzate was isolated in the same way.

3. Description of Experiments

Hydrogenation. Experiment 1. The amount of hydrogen absorbed by 11.5 g (15.4 ml) of isopropenylcyclopropane in presence of 0.4 g of platinum black was 4060 ml (1.3 mol. prop.)* (one molecular proportion of hydrogen would be 3135 ml). The yield of catalyzate was 10.7 g (15.3 ml). The fractionation results are given in Table 2.

Judging from the constants of the fractions given in Table 2, addition of 1.3 molecular proportions of hydrogen to isopropenylcyclopropane gives a mixture of isopropylcyclopropane and 2-methylpentane. The fractions of Experiment 1 were mixed together and the Raman spectrum of the mixture was determined:

$\Delta\nu$ (cm^{-1}) 167(1), 229(2), 279(1), 296(3), 322(1), 339(4), 386(1), 444(2), 464(6), 503(0), 692(1), 708(3) 737(7), 793(2), 815(5), 873(8, sh), 904(3, b), 921(2, background), 952(4), 1010(2,b), 1040(3,b), 1066(1), 1099(3,b), 1123(4,b), 1172(2, diffuse), 1193(9, sh), 1219(3), 1239(2, background), 1290(3,b), 1311(3,b), 1336(2,b), 1367(2), 1388(5, b), 1426(4), 1446(6,b), 1460(6,b).

Experiment 2. The amount of hydrogen absorbed by 22.6 g (30.0 ml) of isopropenylcyclopropane in presence of 0.4 g of platinum black was 4000 ml (0.65 mol. prop.) (one molecular proportion of hydrogen would be 6160 ml). The yield of catalyzate was 21.3 g (30.0 ml). The fractionation results are given in Table 3.

Judging from the data in Table 3, the catalyzate may contain all of the hydrocarbons listed in Table 1. Raman spectra:

* In all experiments the volume of hydrogen is reduced to STP.

Mixture of Fractions I and II:

$\Delta\nu$ (cm^{-1}): 299(5), 341(5), 445(2,b), 467(8,b), 710(4), 739(10,sh), 800(4,sh), 818(5, b), 874(10), 908(4, background), 954(4), 984(1), 1018(½), 1042(4,b), 1068(0), 1094(2, background), 1105(2, background), 1124(4, background), 1164(1), 1175(1), 1194(10), 1212(1, background), 1221(4), 1240(2), 1289(2, background), 1315(5, background), 1336(2,b), 1391(7, sh), 1429(5,sh), 1454(7,b), 1469(7,b), 1653(2,b). [923(3, background), also recorded].

Fraction IV:

$\Delta\nu$ (cm^{-1}): 234(2,b), 267(6,b), 333 (1), 356(1), 394(4), 415(5), 474(9, sh), 485(2), 530(4,b), 656(0), 695(2,b), 713(7,sh), 730(4), 762(0), 794(2,b), 818(5,b), 841 (1), 888(9,b), 901(9, sh), 961(9, sh), 995(4, sh), 1021(4), 1087(4), 1098(4), 1172(2,b), 1193(10,b), 1237(3, v.b.), 1294(5 sh), 1315(0), 1342(2), 1379(4), 1427(6,b), 1461(6,b), 1506(0), 1635(10, sh), 1650(10, sh), 1674(2,b), 1701(0).

TABLE 2

Fraction No.	B.p. (°C)	Amount (g)	n_D^{20}	d_4^{20}	Aniline point (°C)
I	58.3—58.4	1.1	1.3843	0.6820	41.7
II	58.4—58.5	1.9	1.3839	0.6904	—
III	58.5—58.6	3.5	1.3830	0.6890	43.5
IV	58.6—59.2	2.5	1.3815	0.6840	—
V	59.2—59.3	0.7	1.3795	—	53.9
Losses	—	1.0	—	—	—

TABLE 3

Fraction No.	B.p. (°C)	Amount (g)	n_D^{20}	d_4^{20}
I	57.6—57.9	3.6	1.3842	0.6940
II	57.9—58.7	6.6	1.3840	0.6927
III	58.7—68.8	3.7	1.3950	0.6959
IV	68.8—70.1	6.7	1.4240	0.7492
Losses	—	0.7	—	—

Fraction III could not be investigated in detail owing to its powerful fluorescence, but visual examination showed that it contained isopropylcyclopropane, 2-methyl-1-pentene, 2-methyl-2-pentene, and a smaller amount of isopropenylcyclopropane.

Experiment 3. The amount of hydrogen absorbed by 21.4 g (29.0 ml) of isopropenylcyclopropane in presence of 0.4 g of platinum black was 5850 ml (about 1 mol. prop.) (one molecular proportion of hydrogen would be 5835 ml). The yield of catalyzate was 19.1 g (27.5 ml). The fractionation results are given in Table 4.

TABLE 4

Fraction No.	B.p. (°C)	Amount (g)	n_D^{20}	d_4^{20}
I	58.5—59.7	13.5	1.3837	0.6800
II	59.7—70.5	4.6	1.4080	0.7175
Losses	—	1.0	—	—

The results of the fractionation indicate that, as in Experiment 2, a mixture of hydrocarbons was obtained. Raman spectra:

Fraction I

$\Delta\nu$ (cm^{-1}): 296(3), 340(4), 385(0), 444(2), 465(7), 615(0), 654(0), 709(3), 738(9), 800(3), 817(6), 873(10), 886(1), 905(4), 923(2), 953(4), 1016(1,b), 1042(3), 1097(2,b), 1122(4), 1194(10), 1210(2), 1219(4), 1239(1), 1287(2,b), 1314(3), 1336(2,b), 1388(6,sh), 1428(5,sh), 1451(6,b), 1465(6,b), 1652(1).

Fraction II:

$\Delta\nu$ (cm^{-1}): 236(1,b), 267(4,b), 323(0), 340(0), 358(0), 395(2), 414(4), 445(1), 473(6,sh), 487(1, background), 530(2, background), 587(0), 696(1), 714(5), 727(2), 736(2), 798(1), 817(5, b), 873(3), 899(8,v.b.), 952(0), 962(6), 995(2), 1020(4), 1043(2), 1063(2), 1088(2,b), 1103(2,b), 1135(2), 1173(2), 1193(10,b), 1219(1), 1241(1), 1265(1), 1294(4), 1306(1), 1339(1), 1381(5,b), 1391(5,b), 1428(8), 1459(8), 1640(10), 1652(10), 1678(8).

When an attempt was made to hydrogenate isopropylcyclopropane under the same conditions over platinum black and over palladium black, no absorption of hydrogen was observed.

Isomerization. Experiment 1. The amount of hydrogen absorbed by 11.5 g (15.2 ml) of isopropenylcyclopropane in presence of 0.4 g of platinum black was 600 ml (0.2 mol. prop.) (one molecular proportion of hydrogen would be 3135 ml). The catalyzate, amounting to 10.2 g (14.0 ml), had b.p. 65.5-69.5° (754.6 mm); n_D^0 1.4122; d_4^{20} 0.7386. Raman spectrum:

$\Delta\nu$ (cm^{-1}): 234(1,b), 267(6), 297(1), 338(1), 394(4), 415(5), 474(8, sh), 486(3, background), 530(3,b), 696(2), 713(7, sh), 728(4), 738(4), 799(2), 818(5,b), 873(5), 894(9,b), 902(10), 963(8), 995(4,sh), 1020(5), 1047(2), 1087(4), 1100(4), 1172(2), 1193(10), 1221(2), 1237(3,4), 1293(5,sh), 1315(1), 1342(3,b), 1380(1), 1393(6,b), 1428(10), 1461(10), 1504(0), 1638(10,sh), 1651(10,sh), 1673(0-1).

Experiment 2. The amount of hydrogen absorbed by 11.4 g (15.2 ml) of isopropenylcyclopropane in presence of 0.4 g of palladium black was 600 ml (0.2 mol. prop.). The catalyzate, amounting to 10.0 g (13.8 ml), had b.p. 66.5-69.6° (754.6 mm); n_D^{20} 1.4175; d_4^{20} 0.7326. Raman spectrum:

$\Delta\nu$ (cm^{-1}): 205(1), 228(1), 266(6,b), 331(1), 352(1), 394(4), 415(5), 474(7), 486(2), 533(3), 695(3), 713(6, sh), 728(4), 786(2), 798(2), 818(6,b), 836(2,b), 889(3), 898(9, b), 962(7), 994(4), 1020(5), 1045(2), 1061(2), 1088(4), 1104(3), 1170(2, background), 1193(10,b), 1221(2), 1240(9,b), 1293(5), 1307(3, background), 1321(2), 1340(3,b), 1377(3), 1387(5, background), 1428(8,b), 1459(8,b), 1510(0), 1636(10), 1650(10), 1676(6,sh).

Experiment 3. The amount of hydrogen absorbed by 11.02 g (16.0 ml) of 2-methyl-2-pentene in presence of 0.4 g of platinum black was 600 ml, the theoretical amount required for complete hydrogenation being 2930 ml. The catalyzate, amounting to 10.0 g (14.7 ml), had b.p. 62.0-66.2° (743.3 mm); n_D^{20} 1.3945.

Experiment 4. The amount of hydrogen absorbed by 5.2 g (7.5 ml) of 2-methyl-2-pentene in presence of 0.4 g of platinum black was 280 ml, the theoretical amount required for complete hydrogenation being 1380 ml. The catalyzate, amounting to 3.9 g (5.5 ml), had b.p. 60.3-60.7° (747.5 mm); n_D^{20} 1.3862.

The fractionation and Raman-spectrum results obtained in Experiments 3 and 4 show that 2-methyl-1-pentene and 2-methyl-2-pentene do not isomerize into one another under the given conditions.

4. Discussion of the Results of the Analysis of the Raman Spectra

In the analysis of the Raman spectra of the fractions, we made use of the frequencies and intensities for isopropylcyclopropane * given above, those for isopropenylcyclopropane and 2-methylpentenes, which we studied previously [1], and also the data in the literature for 2-methylpentane prepared under conditions similar to ours [5].

* For analysis accurate to within ± 5-10%, an admixture of 2-3% of 2-methylpentane in the isopropylcyclopropane could not have a substantial effect on the results of quantitative analysis.

The determination of 2-methyl-1-pentene in presence of isopropenylcyclopropane presents great difficulties, for when its content is low the only line remaining suitable for photometric estimation is 1651 (76), on which the line 1649 (90) of isopropenylcyclopropane is superimposed. In such a case the 2-methyl-1-pentene content of the fraction can be estimated only very approximately from the increase in the intensity of the line 1649. Most of the intense analytical lines of 2-methylpentane coincide with lines of 2-methylpentenes and cyclopropanes, which makes its determination in mixtures very difficult. For this reason, in all experiments except that on the addition of 1.3 molecular proportion of hydrogen the 2-methylpentane content was determined by difference after the contents of the remaining components had been found. Hence, the analytical results are most reliable for the main components of the fractions – isopropyl- and isopropenyl-cyclopropanes – and also for 2-methyl-2-pentene.

The contents of the individual components of the catalyzates obtained in Experiments 1, 2, and 3 on hydrogenation and Experiments 1 and 2 on isomerization are given in Table 5.

TABLE 5

Catalyst	Amount of hydrogen added (molecules per molecule of hydrocarbon)	B.p. (°C)	Composition of catalyzate (%)					Accounted for (%)
			Isopropenyl-cyclopropane	Isopropyl-cyclopropane	2-Methyl-1-pentene	2-Methyl-2-pentene	2-Methyl-pentane	
Pt	1.3	58.3-59.3	–	70	–	–	30	100
Pt	1.0	58.5-59.7	–	80	3	–	17	100
		59.7-70.5	50	24	?	14	?	88
Pt	0.65	57.6-58.7	–	82	3	–	15	100
		58.7-68.8	+	++	++	++	–	–
		68.8-70.1	85	–		5	–	90
Pt	0.2	–	72	25	–	3	–	100
Pd	0.2	–	80	–	–	20	–	100

SUMMARY

1. It was found that, in the hydrogenation of isopropenylcyclopropane in alcoholic solution at room temperature and atmospheric pressure in presence of platinum black, 1.3 molecular proportions of hydrogen are added and a mixture of 70% isopropylcyclopropane and 30% 2-methylpentane is formed.

2. It was shown that the 2-methylpentane present in the catalyzate is formed under these conditions by the hydrogenation of 2-methyl-1-pentene and 2-methyl-2-pentene formed as intermediate products.

3. It was shown that isopropylcyclopropane is not hydrogenated under these conditions.

4. It was found that isomerization of 2-methyl-1-pentene and 2-methyl-2-pentene into one another does not occur in presence of platinum, whereas such isomerization was observed in experiments with palladium black.

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INVESTIGATION OF THE COMPOSITION OF THE NAPHTHENE PART OF THE KEROSENE FRACTION OF TUIMAZIN (DEVONIAN) PETROLEUM

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The investigation of the hydrocarbon composition of sulfur-containing petroleums is associated with considerable difficulties in that the selective removal of sulfur compounds is accompanied by the loss of an appreciable amount of aromatic hydrocarbons [1]. Naphthene hydrocarbons, which form one of the main hydrocarbon components of most petroleums, have not yet received adequate study, particularly for fractions boiling above 150°. The more detailed study of the hydrocarbons of this class is, however, of great scientific and practical importance.

EXPERIMENTAL*

In the present work we studied naphthenes of the decalin and cyclohexane series by the method of analytical dehydrogenation [2] with subsequent isolation and identification of the aromatic hydrocarbons formed. The kerosene fraction (b.p. 180-310°) of Tuimazin (Devonian) petroleum was subjected to dearomatization and simultaneous desulfurization by five successive treatments under cooling with an equal volume of 100% sulfuric acid. The neutralized, washed, and dried product was passed through a column of silica gel (100-150 mesh) in order to remove traces of resinous and sulfur-containing compounds. The dearomatized kerosene was not fractionated into narrow fractions since preliminary experiments had shown that the secondary aromatics isolated from narrow fractions of the dehydrogenation product did not contain condensed aromatic hydrocarbons. The product, now free from aromatics and sulfur compounds, was treated with urea in the way described previously [3] in order to remove paraffins, and it was then subjected to exhaustive dehydrogenation over a platinum-iron catalyst. The properties of the kerosene after successive removals of individual classes of hydrocarbons are given in Table 1.

Part of the dehydrogenation product was fractionated into fractions corresponding in boiling point to naphthalene and its homologs, the possibility of the formation of azeotropic mixtures being taken into account [4]. Preliminary experiments showed that treatment of the narrow fractions of the dehydrogenation product with picric acid did not yield picrates, and the secondary aromatic hydrocarbons separated on silica gel had low refractive indices and densities characteristic for monoalkyl derivatives (Table 2). The data in Tables 1 and 2 enable us to conclude that decalin and its homologs are absent in the kerosene of Tuimazin petroleum. For this reason the further separation of aromatic hydrocarbons from the dehydrogenation product was carried out on the wider kerosene fraction (b.p. 182-310°).

Study of the ultraviolet absorption spectrum of the dehydrogenation product from Tuimazin kerosene showed that it contained some naphthalene hydrocarbons, but their content in the aromatic fractions was very small, varying from 0.01 to 0.001%. This low content of condensed aromatic hydrocarbons lies outside the limits of the picrate method. It is therefore to be recommended that the determination of very small amounts of naphthalene and its homologs in fractions by the picrate method be carried out on the aromatic concentrates.

In the study of the cyclohexane hydrocarbons of the kerosene fractions of Tuimazin petroleum by the methods of dehydrogenational catalysis, it was shown that the analytical dehydrogenation of these fractions was complicated by side reactions, which resulted in the formation of unsaturated compounds and the elimination of methyl groups [5-8]. However, the part played by these reactions was relatively insignificant. The product obtained by the dehydrogenation of a wide kerosene fraction, b.p. 195-300, at 305-310° with a space velocity of 0.5-0.62 hour^{-1} had an iodine value of 6-7. In order to determine the effect of the space velocity on the extent to which

*Senior laboratory workers I. S. Genekh and P. A. Nikitina took part in the experimental work.

TABLE 1

Properties of Kerosene at Different Stages of its Investigation

Name of Product	Boiling range (°C)	d_4^{20}	n_D^{20}	Amount of		Freezing point (°C)
				Sulfonatable hydrocarbons (%)	S (%)	
Original kerosene	182-310	0.8243	1.4625	25.2	0.78	−24
Dearomatized kerosene	183-292	0.7864	1.4367	0	0	−28
Product after removal of aromatics and paraffins	195-300	0.8040	1.4435	0	0	−56
Dehydrogenation product	180-330	0.8108	1.4524	16.0	0	–

TABLE 2

Properties of Fractions of Dehydrogenation Product

Boiling range (°C)	d_4^{20}	n_D^{20}	Amount of sulfonatable hydrocarbons (%)	Properties of aromatic hydrocarbons separated on silica gel		
				Boiling range of aromatic hydrocarbons (°C)	d_4^{20}	n_D^{20}
180-210	0.7809	1.4356	13.7	160-203	0.8633	1.4940
210-235	0.7994	1.4447	11.3	170-232	0.8840	1.5040
235-270	0.8095	1.4509	12.2	240-320	0.8985	1.5120
270-300	0.8194	1.4569	16.0	230-325	0.8990	1.5110
> 300	0.8295	1.4635	33.8	270-333	0.9000	1.6028

side reactions occurred, the wide kerosene fraction was dehydrogenated at various space velocities: 1.0, 0.75, 0.65, and 0.50 hour^{-1}. The results showed that, irrespective of space velocity, the dehydrogenation product contained unsaturated compounds and the gas contained methane hydrocarbons.

The kerosene fractions are more complex in chemical composition than the gasoline fractions and their dehydrogenation proceeds with greater difficulty. Even after being passed repeatedly over the catalyst at a space velocity of 0.9-1.0 hour^{-1}, the kerosene fractions were only slightly dehydrogenated. Under these conditions a considerable change was generally observed in the temperature conditions in the reaction zone, so that the initial temperature had to be 30-35° higher than usual. The product obtained before stationary temperature conditions were established (305-310°) was disregarded, and after that the dehydrogenation product was collected.

The presence of unsaturated compounds in the dehydrogenation product and of methane hydrocarbons in the gas (Table 3) shows that the dehydrogenation of Tuimazin kerosene over a platinum-iron catalyst is complicated by destructive side reactions that are independent of space velocity.

It follows from the data presented in Table 3 that the contents of methane hydrocarbons in the gas and the iodine values of the dehydrogenation products are almost constant. The maximum content of aromatic hydrocarbons in the dehydrogenation product was obtained at a space velocity of 0.65 hour^{-1}. For the preparation of the fractions for investigation, the product, freed from aromatic hydrocarbons and normal paraffins, was subjected to exhaustive dehydrogenation at a space velocity of 0.65 hour^{-1} under the conditions described above. Two dehydrogenation treatments on 1500 g of product gave 1440 g of the dehydrogenation product (96% yield, 4% loss). The dehydrogenation product had the following properties: d_4^{20} 0.8095; n_D^{20} 1.4524; iodine value 5.7; content of sulfonatables 16.0%; content of aromatics 12.7%.

TABLE 3

Effect of Space Velocity on the Formation of Unsaturated and Methane Hydrocarbons

Space velocity ($hour^{-1}$)	n_D^{20}	Iodine value	Content of aromatic hydrocarbons (%)	Analysis of gas	
				H_2 %	C_nH_{2n+2}
1.00	1.4491	6.8	6.3	96.0	4.0
0.75	1.4497	8.0	8.0	—	—
0.65	1.4510	6.5	10.0	95.5	4.5
0.50	1.4512	6.6	—	94.0	6.0

Chromatography of the dehydrogenation product was carried out in a column of ASM silica gel (Voskresensk Chemical Combine; 100-150 mesh; activity to benzene 14) by the method described previously [9]. The intermediate fraction, separated on silica gel after the petroleum ether distillate, had an iodine value of 75 and was studied in detail. Only secondary aromatic hydrocarbons were investigated. Our previous investigations have shown that aromatic hydrocarbons boiling over a very narrow range (1-3°) can be multicomponent mixtures which give several fractions with different refractive indices when subjected to chromatography on silica gel. For the separation of these aromatic hydrocarbons advantage was taken of the fact that each type of these hydrocarbons has its own characteristic range of refractive indices. By repeated fractionation on silica gel a series of fractions was obtained in narrow ranges of refractive indices; the properties of these fractions are given in Table 4. The further separation of each of these fractions according to boiling point was not practicable owing to their small amounts. The densities and refractive indices of the first ten fractions (Table 4) are very close to the corresponding values given in the literature for alkyl derivatives of benzene [10]. Apart from polyalkylbenzenes, the other fractions probably contain more complex structures, as indicated by their higher densities and refractive indices. It should be noted that, on standing, the fraction of b.p. 292-302° (n_D^{20} 1.5279) gave a small amount of crystalline precipitate, which we did not succeed in extracting from the thick mass for identification. When this fraction was cooled strongly, no increase in the amount of the solid was observed. A chloroform solution of the crystalline product was treated with benzaldehyde in presence of sulfuric acid and gave first a green, and then a stable reddish-violet, coloration, characteristic for acenaphthene [11]. In order to study the ultraviolet absorption spectrum of this fraction, a solution was prepared in isooctane in which the crystals dissolved and the thick yellow mass remained insoluble. A well defined absorption spectrum, identical with that of pure acenaphthene, was obtained (Fig. 1; the spectrum of acenaphthene was determined previously on the same spectrograph under the same conditions). The identification of the aromatic hydrocarbons formed after the dehydrogenation of Tuimazin kerosene by chemical methods was not carried out owing to the small amount of product and its complex composition (Table 4).

The investigation of the compositions of the types of secondary aromatic hydrocarbons was carried out with the aid of ultraviolet absorption spectra. The absorption spectra of aromatic fractions in the near ultraviolet were determined by the method of photographic photometry. The spectra were photographed on a medium quartz spectrograph. The weakening of the light passing through the solution was carried out with the aid of a rotating sector. The absorption spectra of the first six fractions of secondary aromatic hydrocarbons from Tuimazin kerosene showed a close resemblance, both with respect to the position of the bands and with respect to their relative intensities (Fig. 2). Since the differences in the spectra of the first three fractions were within the limits of error of measurement, the absorption spectra of Fractions I-III are represented by a single curve in Fig. 2. The most intense maxima are at wavelengths of 2650 and 2685 A; notable maxima occur at 2600, 2620, and 2730 A; also, at 2780 A is a point of inflection (shoulder) that is characteristic for all five absorption spectra. The positions and forms of the absorption bands indicate that the fractions are substituted benzenes.

The absorption spectra of subsequent fractions are similar in form to those of the first six fractions. From Fraction I onwards, the absorption spectra were calculated with the aid of characteristic curves (without taking account of the contrast factor for different parts of the spectrum). This method of calculation somewhat modified

TABLE 4

Properties of Aromatic Fractions Isolated after Repeated Separation on Silica Gel

Fraction	n_D^{20}	d_4^{20}	Molecular weight	B.p. (°C)
I	1.4820	0.8682	198	242.5—287.0
II	1.4925	0.8700	193	207.0—275.0
III	1.4835	0.8704	183	213.5—275.5
IV	1.4850	0.8735	188	222.0—300.0
V	1.4880	0.8730	205	250.0—285.0
VI	1.4890	0.8745	174	212.0—236.0
VII	1.4963	0.8755	189	221.0—301.0
VIII	1.4977	0.8772	181	210.0—281.0
IX	1.4997	0.8811	170	212.5—251.0
X	1.5024	0.8854	178	208.0—262.0
XI	1.5053	0.8875	—	200.0—235.0
XII	1.5055	0.8899	197	237.0—288.0
XIII	1.5107	0.8957	175	205.0—275.0
XIV	1.5200	0.9073	153	205.0—250.0
XV	1.5332	0.9254	151	202.5—263.0
XVI	1.5411	0.9328	—	220.0—256.0
XVII	1.5577	0.9577	171	230.0—270.0
XVIII	1.5672	0.9636	—	Residue
XIX	1.5725	0.9735	—	Residue

the form of the absorption curve. The absorption spectra of Fractions VII and VIII have in general the same peculiar features as those observed in the spectra of the preceding fractions (Fig. 3).

Comparison of the absorption spectra of eight fractions of Tuimazin kerosene with the spectra of pure alkylbenzenes showed that these fractions contained alkylbenzenes in which the substituents occupied different positions. In order to determine the presence of one or other type of alkylbenzene, not only were the positions of the maxima and their relative heights taken into account, but also the absolute values of the absorption coefficients for each type of alkylbenzene. It is known [12] that monoalkylbenzenes have the lowest absorption coefficients, o- and m-dialkylbenzenes have somewhat higher values, and p-di-, 1,2,4-tri-, and 1,2,4,5-tetra-alkylbenzenes have extremely high absorption coefficients; 1,2,3-tri-, 1,3,5-tri-, 1,2,3,4-tetra-, 1,2,3,5-tetra-, penta-, and hexa-alkylbenzenes have absorption coefficients of the same order as the o- and m-dialkylbenzenes. In the paper [13], which is devoted to an investigation of polyalkylbenzenes containing 9-10 carbon atoms, data are given on the ultraviolet absorption spectra of 15 pure alkylbenzenes boiling in the range 150-180°. The absorption spectra of these hydrocarbons are classified according to types: Type A, monosubstituted; Type B, m- and o-di- and 1,2,3- and 1,3,5-tri-substituted; Type C, p-disubstituted and 1,2,4-trimethylbenzene. Each of these types is characterized not only by the constancy of the positions of the principal absorption maxima, but also by close mean values of the absorption coefficients for all absorption bands.

In order to interpret the absorption spectra of fractions of secondary Tuimazin aromatic hydrocarbons, use was made of the data in the paper [13] and data in the literature on the absorption spectra of alkylbenzenes boiling in the range 100-300° [12,14-20]. It was found that the positions of the absorption maxima and mean values of ε_λ for alkylbenzenes boiling in the range 100-300° are constant, so that the mean "type" absorption spectra established in the paper [13] may be used to establish the main types of substitution of the alkylbenzenes in the fractions boiling in the range 200-300°. The problem of determining the relative amounts of the various types of alkylbenzenes in the kerosene fractions investigated is at present insoluble, since the available data on the absorption spectra of the individual aromatic hydrocarbons are extremely incomplete and have been obtained with various types of apparatus.

The ultraviolet absorption spectra of fractions of the dehydrogenation product of Tuimazin kerosene indicates the presence of the following benzene homologs:

1) monoalkylbenzenes, mainly having branched alkyl chains (maximum 2600 A, shoulder 2540-2550 A);

2) p- and m-dialkylbenzenes (maxima 2600, 2650, 2680, and 2730 A);

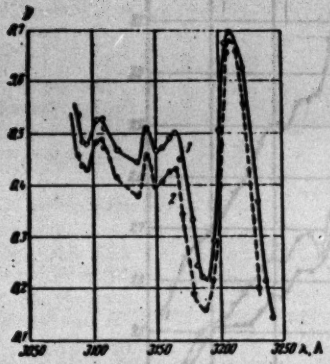

Fig. 1. Absorption spectra: 1) pure acenaphthene; 2) acenaphthene fraction.

3) 1,3,5-trialkylbenzenes (maxima 2625, 2650, 2680 A);

4) 1,2,3,5- and 1,2,3,4-tetraalkylbenzenes (maxima 2680, 2730, 2770 A and 2650, 2680, 2735, 2780 A, respectively).

From the absorption spectra none of the following were detected in the fractions of secondary Tuimazin aromatics: o-dialkylbenzenes, 1,2,4- and 1,2,3-trialkylbenzenes, 1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene.

Some fractions (II-V, VII-X), which were available in amounts of 6-8 ml, were investigated with the aid of Raman spectra. As a rule, the higher gasoline fractions are already becoming difficult to investigate by means of Raman spectra owing to their bright fluorescence. However, the Raman spectra of the kerosene fractions had an insignificant background, so that up to 30-40 lines could be measured in their spectra. It is possible that repeated passage of the product through silica gel had freed it from the impurities causing the fluorescence.

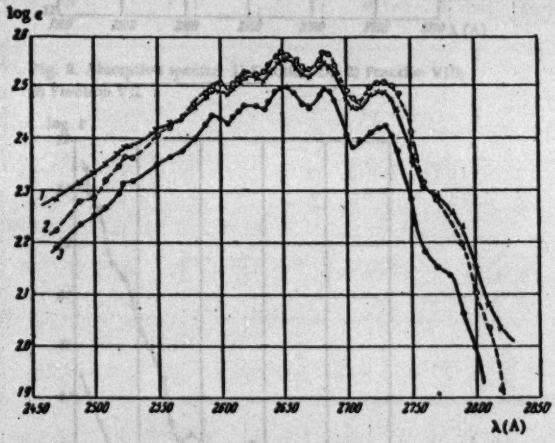

Fig. 2. Absorption spectra: 1) Fraction VI; 2) Fraction IV; 3) Fractions I-III.

The Raman spectra of all the investigated fractions contained lines of the same frequencies and similar intensities, which indicates the closeness of the fractions in composition (Table 5). Analysis of the Raman spectra showed that the fractions of secondary Tuimazin aromatic hydrocarbons contained a small amount of monoalkylbenzenes, some m- and p-dialkylbenzenes, and some polyalkylbenzenes. No. 1, 2,3-trialkylbenzenes were detected by the Raman spectra, and no o-dialkylbenzenes could be found. Hence, the conclusions derived from absorption spectra concerning the principal types of alkylbenzenes present in the fractions of secondary aromatic hydrocarbons are in close accord with those derived from the Raman spectra.

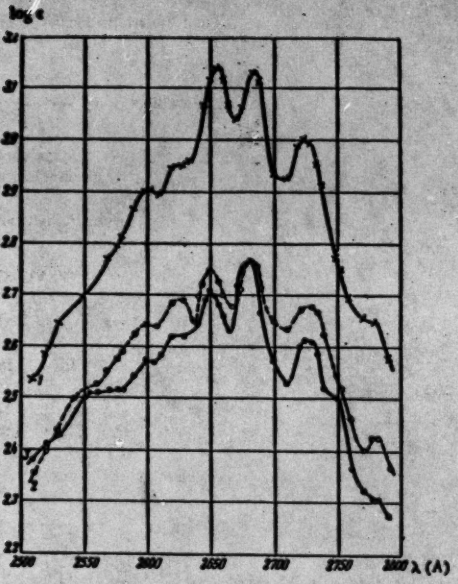

Fig. 3. Absorption spectra: 1) Fraction IX; 2) Fraction VIII; 3) Fraction VII.

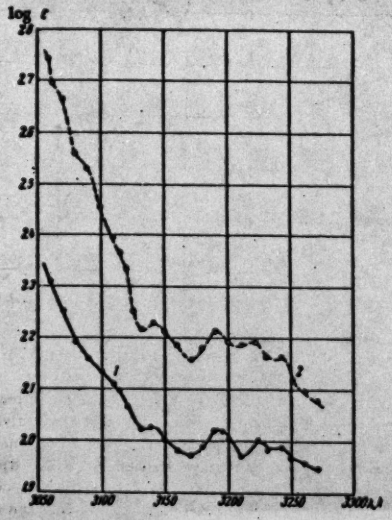

Fig. 4. Absorption spectra: 1) Fraction XV; 2) Fraction XVII.

TABLE 5

Analysis of the Raman Spectra of Fractions of the Secondary Aromatic Hydrocarbons of Tuimazin Kerosene

Aromatic fraction	Monosubstituted [22]	m-Disubstituted [22]	o-Disubstituted [22]	p-Disubstituted [22]	1,2,4-Trisubstituted [22]	1,3,5-Trisubstituted [22]	1,2,4,5-Tetrasubstituted (durene) [23]	1,2,3,4-Tetrasubstituted (prehnitene) [23]	1,2,3,5-Tetrasubstituted (isodurene) [23]	Pentamethylbenzene [23]	Hexamethylbenzene [23]
224 (1,d)											
262 (0,5)									232(7)		229(1)
321 (0)							293(6)	295(5)			
458 (0)								322(6)			
502 (0)								453(7)			
520 (1)							508(9)	510(5)		453(8)	455(2)
552 (1,d)											508(1)
586 (1,db)											
620 (2,sh)	615(VI)										550(8)
642 (1,5)									573(12)	588(10)	
678 (0)				640(IV)				641(11)			
715 (1,5)		716(II)	710(I)		735(I)					652(7)	
739 (2,b)											
804 (1,d)				800(I)			735(10)		736(8)		
839 (1,d)											
1000 (10,sh)	1000(I)	1000(I)				1000(I)					
1030 (3)	1030(III)		1035(II)								
1054 (1)											
1062 (1)											
1080 (0)*											
1106 (2,d)*											
1118 (1,d)*											
1158 (2)			1160(V)								
1182 (0)*											
1203 (3,b)	1200(IV)			1200(II)	1185(IV)						
1244 (1)		1245(III)	1215(III)		1245(II)			1258(10)			
1280 (0)*							1282(8)				
1294 (2)											
1302 (2)						1296(II)			1293(9)	1290(8)	1284(9)
1335 (1)											
1347 (1)											
1381 (2)											
1440 (5,b)							1380(7)	1384(7)	1380(9)	1382(7)	1385(2)
1456 (4,b)											
1555 (0,d)							1449(4,b)				
1583 (1)	1585(V)	1595(V)					1560(4,b)				
1610 (6)	1604(II)	1610(IV)	1605(IV)					1586(5)			
1616 (4)				1615(III)	1625(III)	1615(III)	1620(5)	1606(5)	1614(7)		

Note: The exciting radiation was the mercury line 4358 A (blue). Intensities were estimated visually and are given in parentheses. sh denotes "sharp", df "diffuse", b "broad", and db "double". In the comparison spectra, the roman numerals in parentheses indicate intensity. The characteristic Raman lines are taken from the paper [22], in which they are represented diagrammatically. The heights of the lines in the spectrum of an individual type of molecule indicate approximate relative intensities. The most intense line in each given spectrum is indicated by the numeral I, a less intense line by II, and so forth. Intensities denoted by the same numerals in different spectra are not comparable. For 1,2,4,5-tetramethylbenzene and all succeeding pure hydrocarbons, intensities are given on a 10-degree visual scale. No lines for 1,2,3-trisubstituted benzenes are found in the spectrum (the line 1600 cm^{-1} is absent). Lines indicated by an asterisk can be explained as Raman lines 2650-3060 cm^{-1} due to violet excitation.

The absorption spectrum of Fraction IX (Fig. 3) has anomalously high absorption coefficients, and the positions of the principal maxima are somewhat different than those for the preceding fractions, which cannot be explained by superposition of the absorption spectra of different alkylbenzenes. In order to determine whether naphthalene and its homologs were present in this fraction, its absorption spectrum was determined in the long-wave region (3000-3300 A) at a concentration of 0.7% by weight. Four absorption maxima were found in the region 3100-3250 A: 3140, 3190, 3220, and 3242 A. Exactly the same maxima were found in the spectra of Fractions X-XIII at concentrations of 0.6% and in the spectra of Fractions XIV-XVII at concentrations of 0.06%. The absorption spectra of Fractions XV and XVII are given in Fig. 4. The observed absorption maxima indicate that the naphthalene homologs detected in these fractions of the dehydrogenation product from Tuimazin kerosene are very close in composition.

By comparing the observed absorption maxima (Fig. 4) with the absorption spectra of individual naphthalene derivatives [21], we found that the Tuimazin secondary aromatic hydrocarbons very probably include 1,6-, 1,7- and 2,6-dimethylnaphthalenes and 1,3,5-trimethylnaphthalene; the possibility is not excluded that 2-methylnaphthalene and 1,2- and 1,3-dimethylnaphthalenes may be present in these fractions. It can be said with certainty that 1,4-, 1,5-, 1,8-, 2,3-, and 2,7-dimethylnaphthalenes are absent in the fractions investigated. The absorption spectrum of Fraction XII differs somewhat from the absorption spectra of the other fractions containing naphthalenes. It may be expected that 1,3,7- and 1,2,5-trimethylnaphthalenes will be present in this fraction. The absorption spectra enable us to make an approximate estimate of the amounts of naphthalenes in the fractions investigated, namely, 0.001% for Fractions IX-XII and 0.01% for Fractions XV-XVII.

The repeated separation of the aromatic hydrocarbons on silica gel ensured that fractions were obtained in narrow ranges of refractive index, and to a considerable extent it concentrated them into types. This facilitated their investigation by means of absorption spectra and enabled us to obtain satisfactory Raman spectra. It is very desirable that in future work separation according to boiling point should be performed on fractions selected according to refractive index.

SUMMARY

1. As it is found that, under the given dehydrogenation conditions, cyclohexane hydrocarbons apparently undergo no appreciable change in structure, it may be considered that the aromatic hydrocarbons obtained correspond to the naphthene hydrocarbons.

2. An investigation by means of ultraviolet absorption spectra of the aromatic hydrocarbons isolated from the dehydrogenation product from the kerosene of Tuimazin (Devonian) petroleum showed that this kerosene contains:

a) alkyl derivatives of cyclohexane, including branched-chain monoalkyl derivatives, p- and m-dialkylcyclohexanes, 1,3,5- and 1,2,4-trialkyl derivatives, and tetraalkyl derivatives, mainly 1,2,3,4 and 1,2,3,5; the possibility of the presence of penta- and hexa-methylcyclohexanes cannot be excluded;

b) hydrogenated acenaphthene (found in Tuimazin petroleum for the first time);

c) decalin and its homologs (about 1% on the total amount of the fractions).

3. No bicyclohexyl and its homologs were detected in the kerosene of Tuimazin petroleum.

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COPOLYMERIZATION OF DIENIC HYDROCARBONS WITH VINYL ETHERS

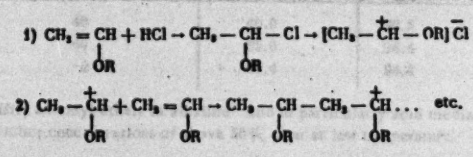
COMMUNICATION 1. PECULIAR FEATURES OF THE COPOLYMERIZATION OF CHLOROPRENE WITH VINYL ETHERS

S. P. Mitsengendler, V. N. Krasulina, and L. B. Trukhmanova

In each of the systems investigated, the component monomers stand at opposite ends of the average-activity series [1]. Chloroprene is the most active of all known monomers: its rate of polymerization is about one thousand times as high as the rates for butadiene and isoprene [2]. This great difference in rate of polymerization and the exceptional tendency for exclusive 1,4-addition to occur are to be attributed to strong polarization of the C=C bonds of the monomer under the action of the chlorine atom. In fact, of all known dienic hydrocarbons and halo hydrocarbons, chloroprene has the highest dipole moment. Chloroprene (M_2) actively copolymerizes both with monomers containing positive substituents (styrene, vinyl ethers) [3,4], and also with monomers containing negative substituents (acrylates) (M_1) [5]. In all cases, chloroprene, being the most active component, predominates in the copolymer, and the copolymers are definitely non-alternating in structure ($r_1 > 1$; $r_2 < 1$). On the other hand, under conditions under which copolymerization proceeds by a cationic mechanism (in presence of Friedel-Crafts catalysts), chloroprene is a component of low activity and makes an insignificant contribution to the copolymer [6].

Alkyl vinyl ethers stand together with vinyl esters in the last group of the average-activity series [1]. In contrast with vinyl esters, the main peculiarity of vinyl ethers is the absence of any tendency to polymerize by the radical mechanism. However, presence of a negative C=C bond tends to cause active copolymerization with monomers containing a positive C=C bond (acrylates, maleic anhydride, acrylonitrile) [7,8]. If there is no polar effect in a system containing alkyl vinyl ethers, copolymerization proceeds extremely slowly, forming products of low weight. It is known that alkyl vinyl ethers can act as polymerization controllers [1,8].

Another important peculiarity of alkyl vinyl ethers is their ability to polymerize very rapidly in presence of traces of hydrogen halide, halides, and catalysts of the Friedel-Crafts type. In a series of investigations, Shostakovsky [9] showed that the polymerization of alkyl vinyl ethers in presence of acids proceeds under the influence of an active molecule that is formed, and a proton-catalyzed process occurs as follows:



The present investigation had the object of studying the effect of chloroprene on the behavior of vinyl ethers under the conditions of radical copolymerization.

EXPERIMENTAL

Chloroprene, prepared in the laboratory, was dried with calcium chloride and distilled through a 1-meter column; b.p. 59.4°. The alkyl vinyl ethers were purified in the usual way [9]; the boiling point of isopropyl vinyl ether was 58.5°. Emulsion copolymerization was carried out at 40° [2] and at from −2 to −5°, using an oxidation-reduction system containing ferrous sulfate, glucose, and pyrophosphate [10]. Homogeneous copolymerization was carried out at 65° in presence of benzoyl peroxide and 2,2'-azobis[2-methylpropionitrile]. The polymerization product was a white mass and was extremely heterogeneous in composition and properties. The product was fractionated by gradual addition of three parts of acetone to one part of a 3-5% benzene solution, and then further gradual addition of methanol. The widest fraction was separated by direct addition of a threefold amount of methanol (Fraction I). In the course of a day a liquid layer separated from the residual solution. After being separated from the solvent and dried, this product was found to be a white elastic macromolecular substance, which contained up to 93-98% of the ether (Fraction II). After the separation of Fraction II, a greasy product containing 0.5-2% of chloroprene (Fraction III) remained in solution. All the fractions were reprecipitated three times, and, after being dried at room temperature in a vacuum, they were analyzed for chlorine content by the Carius method. In special cases the products were fractionated. The molecular weights of the separate fractions were determined with an osmometer.

I. Low-temperature Emulsion Copolymerization

An investigation of the emulsion copolymerization of chloroprene and isopropyl vinyl ether (Table 1) showed that chloroprene copolymerizes very rapidly with vinyl ethers and predominates in the copolymer, which is in accord with the values of the copolymerization constants r_1 and r_2 for this system. As required by modern theory, the compositions of the copolymers vary little with the copolymerization temperature (by about 2%) (Table 2).

TABLE 1

Composition of Copolymers Obtained in the Oxidation-Reduction System at −2°

Composition of original mixture (mole %)		Duration of polymerization (hours)	Yield of copolymer (%)	Composition of copolymer (mole %)	
Chloroprene	Ether			Chloroprene	Ether
50	50	3.0	17.5	94.5	5.5
50	50	17.0	47.4	94.4	5.6
66	34	19.0	67.3	96.3	3.7
75	25	4.5	13.0	96.2	3.8

TABLE 2

Effect of Temperature on the Compositions of Copolymers Obtained by the Emulsion Method.

Composition of original mixture (mole %)		Temperature (°C)	Yield of copolymer (%)	Composition of copolymer (mole %)	
Chloroprene	Ether			Chloroprene	Ether
50	50	40	40.0	96.5	3.5
50	50	40	35.0	96.4	3.6
50	50	−2	47.4	94.4	5.6

Owing to the instability of vinyl ethers in alkaline* and in particularly acid media, it was impossible to carry out investigations at ether concentrations of above 50%, even at low temperature.

* According to data in the literature [2], the pH of the aqueous phase is always lower by 2-3 units after the reaction owing to the elimination of a very small amount of hydrogen chloride.

II. Homogeneous Copolymerization

1. Anomaly observed in the mass copolymerization of chloroprene with alkyl vinyl ethers. The first experiments on the mass copolymerization of chloroprene with isopropyl vinyl ether and with ethyl vinyl ether showed that, unlike emulsion copolymerization, this process does not proceed by a radical mechanism. For almost any proportions of the components, the inactive ether monomer predominates over the active chloroprene monomer in the copolymer. For example, for equimolecular proportions of monomers, the chloroprene content of the copolymer is 22-36%, as against 95% for emulsion copolymerization (Table 3).

TABLE 3

Homogeneous Copolymerization of Chloroprene and Isopropyl Vinyl Ether at 65°.

Composition of original mixture (mole %)		Time (hours)	Yield (% by weight)	Mean composition of copolymer (mole%)	
Chloroprene	Ether			Chloroprene	Ether
9	91	24.0	63.5	11.4	88.6
20	80	–	20.0	20.3	79.7
34	66	2.0	57.0	8.8	91.2
50	50	2.0	25.5	21.8	78.2
50	50	12.0	41.2	36.0	64.0
66	34	2.0	25.1	32.3	67.7

In contrast to the case of radical copolymerization, the compositions of the copolymers were extremely unstable and changed according to the polymerization conditions. For example, presence of air in the system resulted in an increased content of the ether in the copolymer. On the other hand, polymerization in a nitrogen atmosphere increased the chloroprene content. A similar change in the composition of the product occurred when benzoyl peroxide was replaced by 2,2'-azobis[2-methylpropionitrile], which gives nitrogen when it decomposes (Table 4).

2. Formation of an "azeotropic" mixture. The course of the process is very interesting when the molar ratio of ether to chloroprene is 4:1. Under these conditions the composition of the product is identical with that of the original mixture at all stages of the transformation, i.e. the components are used up in a uniform manner during the process and an "azeotropic" copolymer formed. At a higher ether concentration, e.g. at a molar ratio of ether to chloroprene of 9:1, the composition of the product is fairly close to that of original mixture. "Azeotrope" formation occurs also in the case of ethyl vinyl ether (Table 5).

3. Comparison of composition curves for radical and cationic copolymerization. Fig. 1 illustrates the different mechanisms of the processes occurring in emulsion and in mass copolymerization of chloroprene with isopropyl vinyl ether. Fig. 2 illustrates the results of Foster [6] on the radical and cationic copolymerization of chloroprene with styrene. For this system the chloroprene content is 88% in the case of radical copolymerization and 7% in the case of cationic copolymerization. As already pointed out, in processes proceeding by the cationic mechanism, chloroprene is extremely inactive as compared with monomers containing electropositive substituents. Comparison of Figures 1 and 2 indicates similar courses for the composition curves of the systems chloroprene-styrene and chloroprene-isopropyl vinyl ether. We may thus conclude that the anomaly observed in the compositions of copolymers obtained by mass copolymerization in presence of benzoyl peroxide is associated with the occurrence of the process by a cationic mechanism (characteristic for catalysts of the Friedel-Crafts type, some cation-forming substances, and also hydrogen acids).

4. Possibility of cationic copolymerization under the conditions of our investigation. Williams and Walker [11] showed that traces of water remain in chloroprene dried with calcium chloride, and these, and also air, have an effect on the polymerization of the chloroprene. The chloroprene that we used was dried with calcium chloride and undoubtedly contained traces of moisture, which, by reaction with the chloroprene, gave rise to the hydrogen chloride referred to above. As is well known, alkyl vinyl ethers polymerize very rapidly in presence of traces of hydrogen chloride. According to Shostakovsky's scheme, the initial polymerization centers are positively charged molecules of the ether. From Foster's data, given above, it is seen that chloroprene is also able to add to a chain that terminates with a carbonium ion, though to a considerably lower extent. These data from the literature enable us to explain the possibility of cationic copolymerization under the conditions of our investigation.

TABLE 4

Effect of Copolymerization Conditions on the Composition of the Copolymer Obtained (molar ratio of chloroprene to ether of 1:1).

Duration of polymerization (hours)	Yield %	Initiator	Atmosphere	Mean composition of copolymer %		Fraction I		Fraction II		Fraction III	
				Chloroprene	Ether	Yield (%)	Amount of chloroprene (%)	Yield (%)	Amount of chloroprene (%)	Yield (%)	Amount of chloroprene (%)
12	41.2	Benzoyl peroxide	Air	36.0	64.0	15.8	89.7	16.2	2.1	9.2	2.9
2	25.5	Benzoyl peroxide	Air	22.0	78.0	8.2	65.5	8.8	1.3	8.5	1.6
2	38.7	2,2'-Azobis[2-methylpropionitrile]	Air	67.0	33.0	25.4	96.0	4.2	8.5	7.2	5.0
33.0	26.8	Benzoyl peroxide	Nitrogen	50.6	49.4	15.4	88.6	8.6	2.0	2.8	2.0
10.5	12.5	Benzoyl peroxide	Nitrogen	38.3	61.7	5.7	81.6	6.8	1.8	---	---

TABLE 5

Constancy of the Composition of the Copolymer for Varying Progress of Reaction for the Case of an "Azeotropic" Original Mixture

Ether	Chloroprene content (mole %)		Yield of product (%)	Note
	of original mixture	of product		
Isopropyl vinyl	20	20.3	20	The experiments were carried out at 60° in presence of benzoyl peroxide
	20	19.6	39	
	20	17.8	85	
Ethyl vinyl	9	9.5	20	
	9	9.7	22	
	20	19.0	15	

5. Fractionation of the copolymerization products. Fractionation of the copolymers showed that they are mixtures of copolymers differing greatly both in composition and in properties and therefore readily separated from one another (Table 4). For equimolecular proportions of the components, one copolymer (Fraction I) corresponds both in composition and in properties to the product of radical copolymerization. The average chloroprene content of this fraction is 65-90%; the copolymer is not soluble in acetone. The second copolymer – the main product – corresponds in composition and properties to the product of cationic copolymerization. The chloroprene content is 1-2%, and the copolymer is readily soluble in acetone (Fractions II and III). The fractionation of the "azeotropic" copolymer is of very great interest: its overall composition is the same as that of the original mixture for all values of the progress of reaction (Table 6).

The copolymer was fractionated into ten fractions (Table 6 and Fig. 3). It was found that the fractionation curve for this "azeotrope" was again typical for a mixture of copolymers varying greatly in composition. The curve for the composition of (I) is typical for a copolymer of a radical type, and the curve for the composition of (II) is typical for a copolymer of a cationic type. The peculiar feature of this process of dual copolymerization is that the component that is inactive for one process is extremely active for the other. This relationship between

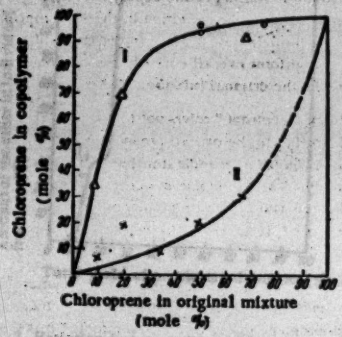


Fig. 1. Composition curves for copolymers obtained: I) in an emulsion; II) in the mass.

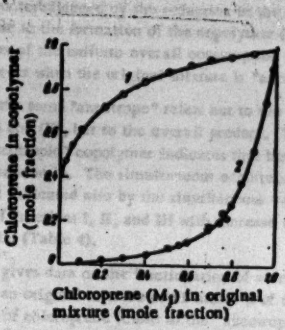


Fig. 2. Composition curves for chloroprene-styrene copolymers (according to Foster): 1) radical copolymerization ($r_1 = 6.3$; $r_2 = 0.005$); 2) cationic copolymerization ($r_1 = 0.24$; $r_2 = 15.6$).

TABLE 6

Fractionation of the "Azeotropic" Copolymer with a Mean Composition of 19.6% of Chloroprene and 80.4% of the Ether.

Fraction	Content of fraction (mole %)	Composition of Fraction		Molecular weight
		chloroprene	Ether	
I	9.05	98.5	1.5	60 000
II	0.67	95.6	4.4	
III	0.73	93.0	7.0	
IV	2.40	74.5	25.5	45 000
V	4.60	69.4	30.6	
VI	1 80	60.5	39.5	
VII	7.60	5.0	95.0	90 000
VIII	34.90	6.2	93.8	
IX	19.20	2.0	98.0	60 000
X	19.25	0.5	99.5	Fluid low-molecular-weight product

the two parallel processes means that, for each of these processes, the concentration of the active component in the original mixture is initially at a minimum and increases during the process.

It may be considered therefore that the minimum chloroprene content on the composition curve for copolymer (I) corresponds to the initial composition of the radical copolymer (I). This composition corresponds to the values obtained for the constants r_1 and r_2 for the radical copolymerization of the system: $r_1 = 0.164$; $r_2 = 11.45$ (Table 7). The minimum content of the ether on the composition curve for the copolymer (II) will probably correspond to the initial composition of the copolymer (II) (these points are marked in Fig. 3 as I_0 and II_0).

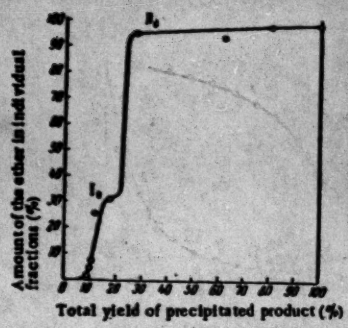


Fig. 3. Variation in composition of fractions during precipitation.

The increase in the consumption of the ether in the course of the process due to the formation of the copolymer (II) is apparently counterbalanced by the reduction in the consumption of the ether due to the formation of the copolymer (I). This is the explanation of the uniform overall consumption of monomers during the process when the original mixture is "azeotropic".

Hence, the term "azeotrope" refers not to the separate copolymers (I) and (III), but to the overall product. The formation of an "azeotropic" copolymer indicates that both processes proceed simultaneously. The simultaneous occurrence of parallel processes is indicated also by the simultaneous variation of the contents of Fractions I, II, and III with increase in the progress of reaction (Table 4).

Table 8 gives data on the fractionation of a copolymer prepared from an original mixture of 91 moles % of the ether and 9 moles % of chloroprene (close to the "azeotropic" mixture).

Fraction III corresponds to the initial composition of the radical copolymer, in accord with the values of the copolymerization contants r_1 and r_2 (Table 7). With increase in the progress of reaction, the radical copolymer becomes enriched in chloroprene (to above 90%) owing to the enrichment of the original mixture in chloroprene, which is again the result of simultaneous cationic copolymerization in which the ether is the main component consumed.

TABLE 7

Experimental Data for the Calculation of r_1 and r_2 for the System at 80° in Presence of 2,2'-Azobis[2-methylpropionitrile] as Initiator.

Experiment	Initial composition of the reaction mixture (mole %)		Yield of copolymer (%)	Chloroprene content of copolymer (mole %)	Final composition of reaction mixture (mole %)	
	Chloroprene M_2^0	Ether M_1^0			Chloroprene M_2	Ether M_1
2	67.78	32.22	36.04	91.90	34.08	30.12
7	19.00	81.00	15.13	69.42	8.74	76.34
6	8.99	91.01	21.44	34.94	1.66	77.83

TABLE 8

Fractionation of a Copolymer having a Mean Composition of 11.4% of Chloroprene and 88.6% of Isopropyl Vinyl Ether; Progress of Reaction 63.5%

Fraction	Precipitant	Yield of fraction (%)	Composition of fraction (moles %)	
			Chloroprene	Ether
I	Acetone	1.0	93.6	6.4
II	Acetone	1.2	91.0	9.0
III	Methanol	18.8	43.5	56.5
IV	"	55.0	2.0	98.0
V	"	24.0	0.5	99.5

Direct Proof of the Simultaneous Occurrence of the Radical and Cationic Mechanisms of Copolymerization

If radical and cationic copolymerization really do take place simultaneously under the conditions of our investigation, then we may direct the process in the desired direction by inhibiting one of the processes. Actually,

when 1% of an inhibitor for radical copolymerization (quinone) was added to a reaction mixture prepared from equimolecular amounts of monomers, then, as in the cationic copolymerization of chloroprene with styrene, a product typical for the cationic mechanism was obtained; the average percentage of chloroprene was 7-12, depending on the progress of reaction (Experiments 2 and 3, Table 9).

TABLE 9

Change in the Direction of the Process, as Affected by the Nature of the Added Inhibitor

Ampoule	Addition of quinone	Addition of alcohol	Duration of polymerization (hours)	Yield of copolymer (%)	Mean composition of copolymer (moles %)	
					Chloroprene	Ether
1	–	–	12.0	41.2	36.0	64.0
2	+	–	15.5	46.2	7.6	92.4
3	+	–	24.0	50.0	12.4	87.6
4*	–	+	6.5	16.8	98.5	1.5
5**	–	+	6.5	32.5	98.3	1.7

* Initiator – 2,2'-azobis[2-methylpropionitrile]; temperature – 80°.

** Emulsion copolymerization.

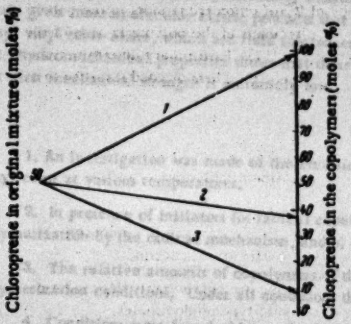


Fig. 4. Dependence of the change of the direction of the process on the nature of the added inhibitor: 1) addition of alcohol (inhibitor for cationic copolymerization); 2) no addition; 3) addition of quinone (inhibitor for radical copolymerization).

When about 10% of inhibitor for cationic copolymerization of alkyl vinyl ethers (alcohol) was added, a copolymer typical for the radical mechanism was obtained, as in emulsion copolymerization (Experiments 4 and 5, Table 9; Fig. 4). This complex process can therefore be controlled so as to obtain macromolecular products enriched with respect to the ether or with respect to chloroprene.

Effect of Chloroprene Units (M_2) on the Activity of the Polymeric Radical of Isopropyl Vinyl Ether (M_1)

A basic assumption of the modern theory of copolymerization is that the activity of the polymeric radical depends only on the structure of the last monomer unit and not on the remaining units in the chain. However, various observations on the hundreds of systems already investigated have indicated that the other units of the chain, particularly the penultimate unit, also have an effect [12-15]. This effect is particularly notable when a monomer containing polar groups is present.

Much earlier, in an investigation of the copolymerization of vinyl acetate (M_1) with maleic anhydride and its derivatives [12-13], one of us showed that the polar monomer unit of vinyl acetate (M_1) affected the activity of the polymeric radical (M_2) and its participation in the formation of the M_2-M_2 link in the copolymer chain. In the radical copolymerization of chloroprene with isopropyl vinyl ether in presence of alcohol we observed an analogous phenomenon: The process is not described by the equation

$$\frac{dM_1}{dM_2} = 1 + \frac{1}{r_2} \cdot \frac{M_1}{M_2}$$

which is for the particular case when $K_{M_1M_1}\delta = 0$, but is described by the equation for the general case with participation of four elementary reactions:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}.$$

The values that we obtained for the copolymerization constants – $r_1 = 0.164 \pm 0.043$ and $r_2 = 11.45 \pm 0.54$ – indicate the considerable activity of the radical (M^0_1), which stands in contrast with its behavior with other monomers. As is well known, in all previously investigated systems in which an alkyl vinyl ether (M_1) takes part, the constant r_1 is zero. In accordance with our calculated values of the constants of the system, it is possible to obtain copolymers containing more than 50% of ether monomer units * (Table 7). It is probable that such a change in the properties of alkyl vinyl ethers is to be attributed to the presence of the strongly polarized chloroprene molecule.

Principal Properties of the New Copolymers Obtained

The copolymers – both those produced by radical copolymerization and those produced by cationic copolymerization – are white elastic substances having molecular weights of 60,000-90,000. An exception is formed by the last low-molecular-weight fraction, which is isolated after removal of solvent; it contains 99.0-99.5% of ether units and 0.5-1% of chloroprene units. Copolymers of both types, when they contain 80-90% of chloroprene in the one case and when they contain 2-6% in the other case, lose their elasticity in the course of time. When they are heated, the elasticity is restored. This is probably to be related to the readiness with which crystallization occurs with formation of a regular structure [16], as in the case of polychloroprene itself. The products of cationic copolymerization are particularly interesting. The presence of 2% of chloroprene units in the polyether chain gives macromolecular elastic products that differ sharply from the products of the polymerization of the alkyl vinyl ether alone, which are fluid substances of low molecular weight [17]. Preliminary determinations of the physicomechanical properties shows that these copolymers are highly elastic rubbers of good stability to oil, but their mechanical strength is extremely low.

SUMMARY

1. An investigation was made of the emulsion and mass copolymerization of chloroprene with isopropyl vinyl ether at various temperatures.

2. In presence of initiators for radical copolymerization, two mechanisms operate simultaneously: a) copolymerization by the radical mechanism, and b) copolymerization by the cationic mechanism.

3. The relative amounts of copolymers of the radical and cationic types are considerably dependent on the polymerization conditions. Under all conditions the copolymer of the cationic type predominates.

4. Conditions were found which make it possible for the process to be directed in a single direction with formation of copolymers containing up to 95-98% of the vinyl ether (molecular weight 60,000-90,000) or 80-90% of chloroprene (molecular weight 60,000).

5. The radical-copolymerization constants of the system were determined: $r_1 = 0.164 \pm 0.043$; $r_2 = 11.45 \pm 0.54$. The existence of two constants is explained as the result of the effect of the penultimate monomer unit (M_2).

6. The emulsion copolymers corresponded in composition to a mechanism of radical copolymerization.

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* Even when alkyl vinyl ethers are copolymerized with acrylic esters, the content of the ether does not exceed 50% [7].

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* T.p = C.B. Translation pagination.

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OPTICAL METHOD OF INVESTIGATING HYDROCARBONS

COMMUNICATION 9.* RAMAN SPECTRA OF SOME NAPHTHENES

P. A. Bazhulin, A. I. Sokolovskaya, N. A. Belikova

A. L. Liberman, and A. F. Plate

In the present communication we present some new data on the Raman spectra of five naphthene hydrocarbons and one aromatic hydrocarbon. Most of these hydrocarbons are difficult to synthesize.

EXPERIMENTAL RESULTS

All the measurements were carried out on an ISP-51 spectrograph with a camera of f = 270 mm. The procedure for the determination of frequencies and intensities was the same as in the preceding papers [1-7].

We give the data on the frequencies and intensities for the six hydrocarbons below. For each hydrocarbon the method of preparation is outlined and its principal constants (boiling point, density, and refractive index) are given. All data on intensities in this communication are expressed on a scale somewhat improved in accuracy [8]. Abbreviations for characteristics of the lines are: b (broad), sh (sharp), bk (line is on background of considerable intensity), db (doublet), (?) (line may be repeat from another exciting frequency).

cis-1-Butyl-2-methylcyclopentane. This was synthesized together with the trans isomer by reaction of 2-methylcyclopentanone with butylmagnesium bromide, dehydration of the alcohol formed, and hydrogenation of the resulting butylmethylcyclopentene in the cold in presence of platinized charcoal activated with palladous chloride. After purification of the product by chromatographic adsorption on silica gel, the mixture of stereoisomers was separated by distillation under reduced pressure through an 80-plate column [9]: b.p. 175° (760 mm); 78.7° (28 mm); n_D^{20} 1.4381; d_4^{20} 0.7980; Found MR 46.15; Calculated for $C_{10}H_{20}$ MR 46.18. The individual stereoisomer was prepared for the first time.

$\Delta\nu$: 277 (8, b), 297 (8, b), 372 (5), 382 (5), 423 (3, b), 460 (1, b), 501 (3), 511 (2), 520 (2), 724 (1), 758 (9), 778 (11), 805 (5), 820 (5), 836 (8), 869 (6), 888 (29, b, db), 922 (12), 960 (0), 980 (10, b), 1018 (8), 1054 (15, db) 1088 (12), 1120 (9), 1150 (5), 1191 (8, b, db), 1240 (2), 1268 (8, b), 1300 (18, b, db), 1350 (4, b), 1446 (50), 1460 (70), 1472 (20, b), 2813 (0), 2855 (150), 2871 (300), 2895 (150, bk), 2908 (280, bk), 2932 (280), 2960 (290).

trans-1-Butyl-2-methylcyclopentane. This was prepared together with the cis isomer and was separated by distillation through an 80-plate column (see above): b.p. 169.4-169.5°; 74.0-74.1° (28 mm); n_D^{20} 1.4321; d_4^{20} 0.7847; Found MR 46.37; Calculated for $C_{10}H_{20}$ MR 46.18. The individual stereoisomer was prepared for the first time.

$\Delta\nu$: 237 (7, b), 248 (7, b), 288 (7, b), 333 (5), 378 (6), 404 (0), 424 (4), 504 (9), 525 (3), 552 (4), 600 (4, b), 762 (2), 777 (7), 798 (2), 813 (6, b) 873 (8, b, db), 895 (24, sh), 905 (10), 925 (3), 987 (2, b), 1001 (8), 1033 (4), 1059 (9), 1084 (11), 1093 (11), 1138 (9, b, db), 1185 (7, b), 1220 (2, b), 1242 (0), 1270 (3), 1296 (13, b), 1343 (8), 1377 (4), 1441 (30), 1450 (50), 1461 (40), 2731 (5, b), 2854 (200), 2868 (300), 2908 (240, bk), 2923 (200, bk), 2940 (240, bk), 2960 (270).

cis-1-Ethyl-4-methylcyclohexane. This was synthesized together with the trans isomer from p-bromotoluene, which was converted into 1-ethyl-4-methylbenzene by the Wurtz reaction, the product being then hydrogenated over platinized charcoal at 175°. The 1-ethyl-4-methylcyclohexane so obtained was then purified by

* Communication 8 was published in Bull. Acad. Sci. USSR, Physics Series [8].

chromatographic adsorption on silica gel, and the cis and trans isomers were separated by distillation through an 80-plate column [10]: b.p. 152.6°; n_D^{20} 1.4374; d_4^{20} 0.7969; Found MR 41.53; Calculated for C_9H_{18} MR 41.56. The individual stereoisomer was isolated for the first time.

$\Delta\nu$: 202(2,b), 305(0), 368(15), 392(3), 410(3), 443(10), 468(5), 489(4), 590(1), 631(31), 738(15,sh), 753(34), 766(15), 781(32), 817(20), 896(4), 909(2), 951(5), 966(10), 1004(10,b), 1028(8), 1044(8), 1059(31), 1103(10,b,db), 1163(19), 1195(6), 1206(6), 1264(37), 1288(3), 1308(3), 1348(19), 1439(46), 1459(46), 2853(220), 2880(100,bk), 2905(100,bk), 2924(200,b), 2930(270,b), 2959(50).

trans-1-Ethyl-1-methylcyclohexane. This was prepared together with the cis isomer and was separated by distillation through an 80-plate column (see above): b.p. 149.1°; n_D^{20} 1.4304; d_4^{20} 0.7798; Found MR 41.85; Calculated for C_9H_{18} MR 41.56. The individual stereoisomer was prepared for the first time.

$\Delta\nu$: 201(0), 242(0), 280(2), 306(5), 345(38), 378(1), 402(2), 441(2), 454(27), 477(23), 508(0), 754(65), 778(43), 841(3), 913(8), 967(5), 991(8), 1014(5), 1031(10), 1069(65), 1108(3,b), 1166(26), 1175(23), 1195(0,b), 1251(41), 1275(2), 1306(11), 1345(24), 1354(30), 1442(36,b), 1457(60), 2672(3,b), 2846(290), 2873(160,b), 2909(160,b), 2932(240), 2959(100,b).

Hexylcyclohexane. This was synthesized by reaction between hexylmagnesium bromide and cyclohexanone, dehydration of the alcohol formed, and hydrogenation of the product in the cold in presence of platinized charcoal activated with chloroplatinic acid. The product was purified by chromatographic separation on silica gel and was vacuum-distilled through a 40-plate column: b.p. 123.5-123.7° (40 mm); n_D^{20} 1.4464; d_4^{20} 0.8077; Found MR 55.61; Calculated for $C_{12}H_{24}$ MR 55.42. The literature [11] gives b.p. 224.0°; n_D^{20} 1.4462; d_4^{20} 0.8076.

$\Delta\nu$: 228(4,b,bk), 255(4,b,bk), 406(2,b), 446(8), 495(0), 510(0), 524(0), 744(2), 776(19), 793(19), 811(4,b), 844(21), 894(4,b), 931(2,b), 979(5,b), 1033(36), 1053(6,bk), 1082(10), 1104(6,b), 1120(6,b), 1157(8,b,db), 1182(2,b), 1203(0), 1261(28,b), 1301(16,b,db), 1348(11), 1366(4), 1393?(2), 1445(75), 1460(10,b), 2667(5,b), 2728(2,b), 2842(260,b), 2853(260,b), 2875(100), 2892(100,bk), 2919(170), 2933(170), 2959(50).

Hexylbenzene. This was synthesized by reaction between pentylmagnesium bromide and benzaldehyde, conversion of the resulting 1-phenyl-1-hexanol into its acetic ester, and pyrolysis of this at 425° into 1-phenyl-1-hexene, which was hydrogenated in the cold over palladized charcoal activated with palladium chloride. The product was vacuum-distilled through a 40-plate column: b.p. 126.8-126.9° (39 mm); n_D^{20} 1.4872; d_4^{20} 0.8576. The literature [11] gives b.p. 226.1°; n_D^{20} 1.4864; d_4^{20} 0.8575.

$\Delta\nu$: 233(25,b,bk), 259(5,b), 353(0,b), 394(0,b), 510(0,b), 526(0,b), 569(2,b), 594(2,b), 622(37), 749(23), 786(10), 802(5), 816(20), 842(6), 864(4), 892(7), 902(8), 938(0), 1003(250), 1031(60), 1065(8), 1076(8), 1113(14,b), 1155(22), 1183(15,db), 1202(38), 1304(24,b), 1339(0), 1444(38,b), 1453(30,b), 1584(20), 1606(65), 2857(110), 2879(60,bk), 2904(130,b,bk), 2935(120,bk), 2965(30), 3050(50,b), 3065(140), 3075(100,b).

DISCUSSION OF RESULTS

In this investigation the Raman spectra of the stereoisomers (cis and trans) of 1-ethyl-4-methylcyclohexane and 1-butyl-2-methylcyclopentane were studied for the first time. Table 1 gives a comparison of the frequencies and intensities of the most intense lines of the cis and trans isomers of 1-ethyl-4-methylcyclohexane.

As can be seen from Table 1, these two stereoisomers have many frequencies in common, but there are some fairly intense lines which differ from one another. The most intense characteristic lines distinguishing one form from the other are: for the cis form 368(15), 631(31), 738(15,sh), 766(15), 817(20) cm^{-1}; for the trans form 345(38), 454(27), 1069(65), 1175(23), 1251(41), 1354(30) cm^{-1}. These data provide a basis for determining the degree of resolution in our preparations, i.e. the presence of one form in the other. A careful examination of these spectra indicated that we had achieved good separation, the spectroscopic data indicating that any contamination of one form by the other amounted to less than 2-3%.

Table 2 gives a comparison of the most intense lines of cis- and trans-1,4-dimethylcyclohexane [7] with those of 1-ethyl-4-methylcyclohexane.

TABLE 1

No.	1-Ethyl-4-methylcyclohexane			
	cis isomer		trans isomer	
	Δν cm⁻¹	I_r	Δν cm⁻¹	I_r
1	—	—	345	38
2	368	15	—	—
3	—	—	454	27
4	—	—	477	23
5	631	31	—	—
6	738	15, sh	—	—
7	753	34	754	65
8	766	15	—	—
9	781	32	778	43
10	817	20	—	—
11	1059	31	1069	65
12	1163	19	1166	26
13	—	—	1175	23
14	1264	37	1251	41
15	1348	19	1345	24
16	—	—	1354	30

From these results it can be seen that, as we pointed out previously [7], replacement of methyl by ethyl in one stereoisomer does not result in substantial changes in frequencies. The most notable changes are in the intensities. For example, the intensity of the symmetrical vibration of the ring at 760 cm^{-1} is reduced for both forms by a factor of 3-4 when methyl is replaced by ethyl. It must be pointed out also that, both for the cis and for the trans form, we observe some fairly intense lines which can probably characterize one of these forms, irrespective of the number of carbon atoms in the side chain. For example, the frequency 630 cm^{-1} is present only in the cis forms and the frequency 454 cm^{-1} is present only in the trans forms. To such frequencies we must assign the frequency 1260 cm^{-1} for the characterization of the cis form and the frequency 1250 cm^{-1} for the characterization of the trans form.

It is characteristic that, when one methyl is replaced by ethyl, the frequency 760 cm^{-1} is lowered by about 6-7 cm^{-1} for both forms. These peculiarities can probably be applied in the solution of some analytical problems met in the investigation of higher-boiling hydrocarbons of the type under consideration.

Table 3 gives a comparison of the frequencies and intensities of the principal lines of the spectra of cis- and trans-1-butyl-2-methylcyclopentane. These isomers have spectra containing many lines, but the intensities are low. It is therefore difficult to establish the presence of one isomer in the other with adequate precision. As can be seen from Table 3, the spectra of the cis and trans forms contain lines which, although weak, are sufficiently intense for differentiation between the isomers. For the cis form such lines are 277 (8,b), 297 (8,b), 836 (8), 888 (29,b,db), 1018 (8), 1120 (9), and for the trans form: 895 (24,sh), 905 (10), 1001 (8), 1093 (11).

TABLE 2

No.	cis-1,4-Dimethylcyclohexane	cis-1-Ethyl-4-methylcyclohexane	trans-1,4-Dimethylcyclohexane	trans-1-Ethyl-4-methylcyclohexane
1	373(17, db)	368(15)	376(65)	345(38)
2	—	—	454(43)	454(27)
3	472(26, db)	468(5)	475(20)	477(23)
4	637(24)	631(31)	—	—
5	—	738(15,sh)	—	—
6	760(130)	753(34)	760(200)	754(65)
7	—	766(15)	—	—
8	788(23)	781(32)	786(8)	778(43)
9	—	817(20)	—	—
10	954(21)	951(5)	953(14)	967(5)
11	1055(31)	1059(31)	1062(95)	1069(65)
12	1263(31)	1264(37)	1250(48)	1251(41)

From these spectroscopic data we may conclude that, if one form is contaminated by the other, then the extent of contamination is probably not greater than 5%. The crudeness of this estimation is due to the low intensity of the analytical lines.

In Table 4 we give a comparison between the intense lines of 1,2-dimethylcyclopentane and 1-butyl-2-methylcyclopentane. It will be seen that the frequencies in the spectrum do not greatly change when methyl is replaced by butyl, but, as for the above-described hydrocarbons, the intensities fall appreciably. The data cited

TABLE 3

No.	1-Butyl-2-methylcyclopentane	
	cis form	trans form
1	277(8, b)	—
2	297(8, b)	—
3	501(3)	504(9)
4	758(9)	762(2)
5	778(11)	777(7)
6	836(8)	—
7	868(6)	873(8, b, db)
8	888(29, b, db)	895(24, sh)
9	—	915(10)
10	922(12)	925(3)
11	980(10, b)	987(2, b)
12	—	1001(8)
13	1018(8)	—
14	1054 (15, db)	1050(9)
15	1068(12)	1084(11)
16	—	1093(11)
17	1120(9)	—
18	—	1138(9, b, db)
19	1191(8, b, db)	1185 (7, b)

TABLE 4

No.	cis-1,2-Dimethylcyclopentane	cis-1-Butyl-2-methylcyclopentane	trans-1,2-Dimethylcyclopentane	trans-1-Butyl-2-methylcyclopentane
1	498 (18)	501 (3)	497 (30)	504 (9)
2	764 (46, db)	758 (9)	766 (20, db)	762 (2)
3	888 (42)	888(29, b, db)	898 (38)	895 (24, sh)
4	1019 (17, b)	1018 (8)	—	—
5	1080 (6)	1088 (12)	1081 (14, b)	1084 (11)
6	(1160 4)	1150 (5)	1147 (11)	1138 (9, b, db)

indicate a fairly stable frequency of the symmetrical vibration of the ring at 888 cm^{-1} for the cis form and 898 cm^{-1} for the trans form. The stability of these lines can be traced also when the methyl group is replaced by ethyl or propyl [3].

With regard to the stability of lines characteristic for a definite class of compounds, hexylcyclohexane and hexylbenzene are not exceptions to this empirical rule. If, for example, we make comparisons between various monosubstituted benzenes, then here also we find that as the methyl of toluene is replaced by other radicals (ethyl, propyl, etc.) a series of extremely stable frequencies is to be observed (622, 1005, 1031 cm^{-1}, and others) with, on the other hand, considerable variations in intensity. For example, as we pass from toluene to hexylbenzene, the intensity of the line at 1005 cm^{-1} is reduced by about one-half.

All the data that we have cited appears to confirm the empirical law considered above. This law can be applied to the establishment of group criteria of value for the analysis of high-boiling hydrocarbons which, for one reason or another, are difficult to synthesize.

In conclusion we take the opportunity of expressing our sincere thanks to G. S. Landsberg and B. A. Kazansky for valuable advice and discussions.

SUMMARY

1. Raman spectra are given for five naphthene hydrocarbons and one aromatic hydrocarbon.

2. It is shown that the cis and trans isomers of dialkylcycloalkanes give lines that are sufficiently characteristic to enable the isomers to be distinguished from one another.

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*T.p = C. B. Translation pagination.

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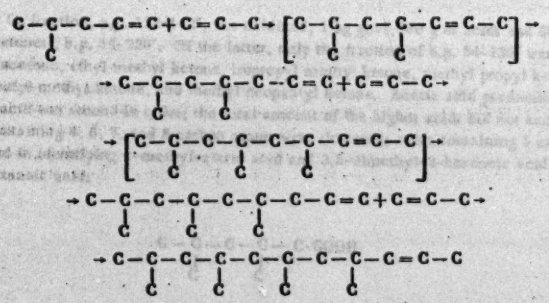
MECHANISM OF

THE CATALYTIC POLYMERIZATION OF PROPENE UNDER PRESSURE

L. I. Antsus and A. D. Petrov

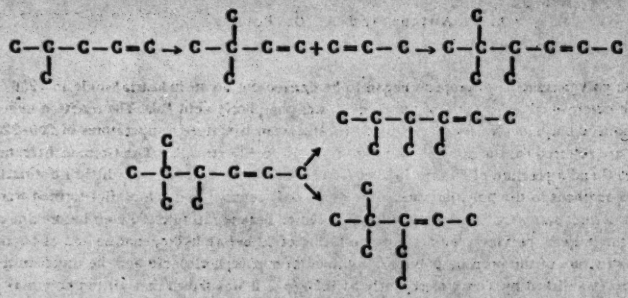
The catalytic polymerization of propene began to be carried out on an industrial scale in 1936, and the catalyst, which had determined the success of the process, was phosphoric acid [1]. The reaction over this catalyst has been carried out under various conditions. In American literature temperatures of 200-220°, and sometimes higher, are referred to, the pressure being from 40-50 to 400 atm [2]. The German literature indicates a temperature of 200° and a pressure of 50 atm [3]. Until very recently there was very little information on the structure of the hydrocarbons in the polymerizate. One could only suppose that the olefins formed were of only slightly ramified structure, since the polymers of butenes have an octane rating of 80 both before and after hydrogenation, whereas the propene polymers have an octane rating of 80 before hydrogenation and of 56 after hydrogenation [4]. The structure of the propene polymers obtained over phosphoric acid and the mechanism of this polymerization were established by Terres as recently as 1953 [5]. It was shown that all the polymers gave only acids when oxidized: the dimer gave acetic and isobutyric acids, the trimer acetic and 2,4-dimethylvaleric acids, the tetramer acetic and 2,4,6-dimethylheptanoic acids, and the pentamer acetic and 2,4,6,8-tetramethylnonanoic acids.

In this case, therefore, the mechanism of the polymerization consists merely in the stepwise addition of propene without isomeric changes:



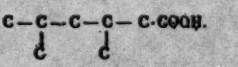
At first, propene polymers obtained over phosphoric acid were used as components of low-octane straight run motor fuels. Later, the main use for these polymers became basic organic synthesis, the most important polymer being the tetramer – the C_{12} fraction: this is used for the alkylation of phenols, the products being plasticizers for nylon, and as a raw material for the manufacture of non-ionic detergents, for which purpose it is condensed with 3-12 molecules of ethylene oxide [6]. The most important application is the preparation of a dodecylbenzenesulfonate from the C_{12} fraction and benzene: this was carried out in Germany during the war [7] and the product has recently received extensive application in the US as a base for detergents [8]. Some years

ago we undertook the study of the polymerization of propene over zinc chloride. This catalyst attracted our attention both because of its lower tendency to corrode, as compared with phosphoric acid, and because of the possibility that more highly branched structures might be obtained. Our hopes were fully justified. In 1950 we reported [9] the establishment of the structures of the nonene isomers in the main C_9 fraction, b.p. 132-136° (the whole of the C_9 fraction boiled over the range 122-142° and was twice the weight of the main fraction). The 133-136° fraction consisted mainly of 3-ethyl-4,4-dimethyl-2-pentene, 3,4,5-trimethyl-2-hexene, and 3,4-dimethyl-3-heptene. These results enable us to conclude that, in the process of condensation with propene, the dimer fraction (consisting of 2-methyl-1-pentene and 4-methyl-1-pentene) first undergoes isomerization into 3,3-dimethyl-1-butene to a considerable extent:

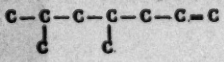


In the present paper we give some supplementary data on the structures of the hydrocarbons of the wide C_9 fraction, and also on the changes in the composition of the polymerizate and in the course of the process resulting from changes in polymerization conditions. The investigation of the wide C_9 fraction showed that it contained not only highly branched hydrocarbons, but also only slightly branched hydrocarbons, and it enabled us to characterize the polymerizate as a complex product arising as the result of a certain equilibrium between polymerization and depolymerization processes.

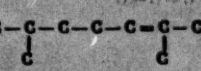
When the wide C_9 fraction, b.p. 122-142°, was oxidized, 1 kg gave 200 g of acids and 609 g of neutral oxidation products (ketones), b.p. 54-220°. Of the latter, only the fraction of b.p. 54-130° was investigated, and in this we identified acetone, ethyl methyl ketone, isopropyl methyl ketone, methyl propyl ketone, isobutyl methyl ketone, sec-butyl methyl ketone, and methyl neopentyl ketone. Acetic acid predominated among the acids, and propionic acid was second in order; the total amount of the higher acids did not exceed 20%, and among them acids containing 4, 6, 7, and 8 carbon atoms were detected; acids containing 5 carbon atoms were absent. We succeeded in identifying 4-methylvaleric acid and 3,5-dimethyl-2-hexenoic acid, clearly formed from 3,5-dimethylhexanoic acid:



A comparison of the oxidation products enables us to conclude that, apart from the compounds already found, the C_9 olefins include also trimethylhexenes, such as 2,3,5-trimethyl-2-hexene (acetone and isobutyl methyl ketone) and some only slightly branched alkenes: 4,6-dimethyl-1-heptene, 2,6-dimethyl-2-heptene, 7-methyl-3-octene, etc. The presence of 4,6-dimethyl-1-heptene

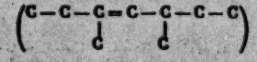


is supported by the formation of 3,5-dimethylhexanoic and formic acids in the oxidation treatment; and the presence of 2,6-dimethyl-1-heptene



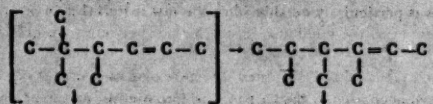
is supported by the identification of 4-methylvaleric acid and acetone. The possibility of the same acid being associated not only with acetone, but also with propionic acid is suggestive of the probability that 7-methyl-3-octene is present.

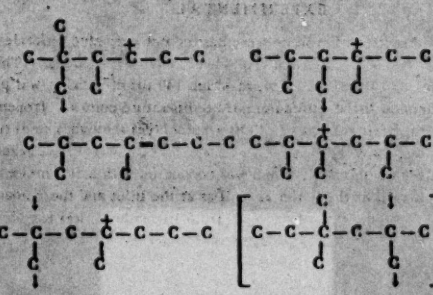
Among the oxidation products formed without breakdown of the C_8 olefin molecule we found not only the previously identified [9] 3-ethyl-3-hydroxy-4,4-dimethyl-2-pentanone, but also 3-hydroxy-3,5-dimethyl-4-heptanone, b.p. 73-75° (10 mm). This hydroxy ketone was clearly formed by the oxidation of 3,5-dimethyl-3-heptene

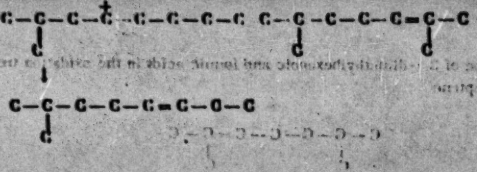


It was identified by oxidation with periodic acid; ethyl methyl ketone was isolated together with an acid of b.p. 173-176°, f.p. below -70°, and silver content of silver salt 51.38%. From the boiling point, freezing point, and silver content of the silver salt we concluded that the acid was 2-methylbutyric acid. The view that it was this acid, and not isovaleric acid, is supported also by the fact that hydroxy ketones can be obtained in the oxidation of olefins only when there is a substituent in the α-position to the carbon at one end of the double bond.

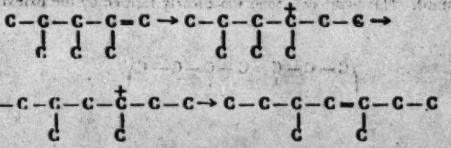
Among the C_8 olefins, the identification of which is still far from complete, the above-mentioned only slightly branched alkenes are of particular interest. Their formation is mainly due to the reverse course of the isomerization, i.e. conversion of highly branched forms into less branched forms. The mechanism of these transformations, with formation, for example, of 7-methyl-3-octene and 2,6-dimethyl-2-heptene, can be represented as proceeding through carbonium ions. It was shown previously that the isomerization of the very important intermediate form 4,5,5-trimethyl-2-hexene leads to 3,4,5-trimethyl-2-hexene:



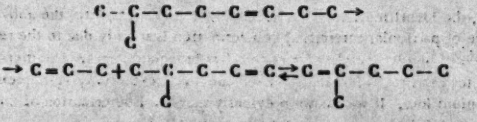




The carbonium ion formed by the addition of a proton to the first of these forms is converted into 4,6-dimethyl-3-heptene as a result of isomerization of the tert-butyl radical into isobutyl. The carbonium ion formed from 4,6-dimethyl-3-heptene is converted into 7-methyl-3-octene by isomerization of 1-methylbutyl into pentyl. The carbonium ion formed from the second converts to 2,6-dimethyl-2-heptene by isomerization of sec-butyl into isobutyl and 1,2-dimethylpropyl into isopentyl. (Apart from the above route for 4,6-dimethyl-3-heptene formation, the possibility of this olefin forming from 4,6-dimethyl-1-heptene, as in Terres's scheme [5], cannot be excluded). Analogously, representation of 3,5-dimethyl-3-heptene formation from the same highly branched form of 3,5,5-trimethyl-2-hexene is not difficult.



The occurrence of the reverse isomerization makes it possible to understand, in particular, the mechanism of the depolymerization of propene polymers and the formation from nonenes of propene, 4-methyl-1-pentene, and 2-methyl-1-pentene, which is observed in some experiments; these are probably formed according to the scheme:



Reverse isomerization of olefins is particularly notable when the raw material is in prolonged contact with the catalyst used when it is desired to raise the yield of macromolecular polymers. Analogous transformation of branched forms into normal forms was noted by Ciapetta and Hunter [10], who showed that 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane are converted into n-hexane over nickel supported by aluminosilicate. The n-hexane is formed by dehydrogenation of the C_6 paraffins into olefins, and the conversion of these through carbonium ions into n-hexane.

EXPERIMENTAL

Experiments on the polymerization of propene were carried out over zinc chloride supported by pumice (ratio 1:1) at a temperature of 200-240° and pressures of 440-400 and 140-100 atm. The reactor consisted of a tube, internal diameter 20 mm and length 470 mm, in which 140 ml of catalyst was placed. The reactor was heated with an electric block furnace fitted with automatic temperature control. Propene was pumped at the pressures indicated from an intermediate reservoir (a 2-liter autoclave) through a steel tube to the upper end of the reactor. The unchanged propene and polymers left at a valve at the exit of the reactor and passed through a condenser to a receiver fitted with a stabilizer which was connected with a flowmeter and gas meter, so that the velocity of gas could be registered at the outlet as well as at the inlet and the amount of gas converted into polymers could be calculated. The same rate of passage, 3-3.5 liters/hour, was used both at 400-440 atm and at 140-100 atm. In the first case the degree of conversion was about 100%, and in the second case about 70%.

In each case the efficiency of the catalyst remained constant over a period of 400 hours. The degree of ramification of the hydrocarbons (as judged by octane values) and the relative amounts of the fractions (about 50% of C_9, 20% C_{10} olefins) were the same in both cases. By increasing the duration of contact by a factor of 2.5-3, we succeeded in raising the yield of the C_{10} fraction to 55% under the normal conditions (100 atm, about 3 liters of propene per hour) the yield of the fraction of b.p. > 150° was 20% and the pressure fell by 40 atm in 5-8 minutes, but when the pressure fell by 40 atm in 20-30 minutes the yield of the fraction of b.p. > 150° was 53-55%.

Investigation of the structures of the C_9 olefins. Oxidation of 1 kg of C_9 olefins gave 200 g of acids. Half of this amount, in the form of a solution of the potassium salts, was subjected to further oxidation under Meyer's conditions [11] with the object of isolating acids containing tertiary carbon atoms. When oxidation was complete, the colorless solution was evaporated to dryness. Salts of organic acids were extracted from the dry residue with alcohol and, after removal of alcohol by distillation, were decomposed with sulfuric acid. The acids were extracted with ether, the ether was removed from the extracted with ether, the ether was removed from the extract, and volatile acids were distilled off with steam.

Investigation of the nonvolatile acids. In order to separate γ- and δ-hydroxy acids from α- and β-hydroxy acids in the mixture obtained by Meyer oxidation, the residue from the distillation of volatile acids was neutralized with sodium carbonate, and the surface layer of oil which then formed was extracted with ether. The product obtained began to boil at 200° and came over completely at 206°; it smelled of honey. In order to confirm that this product was a lactone, it was boiled with baryta water; the honey odor disappeared and the barium salt of the acid was precipitated. The barium salt was converted into the silver salt by double decomposition with silver nitrate; the silver content 45.31% corresponded to $C_6H_{11}O_2Ag$, the silver salt of a hydroxy acid.

From the above-described properties of the hydroxy acid we may conclude that 4-methylvaleric acid is present in the acid products of the oxidation of the wide fraction of C_9 olefins; it could be formed by the oxidation of two of these olefins; 2,6-dimethyl-2-heptene and 7-methyl-3-octene.

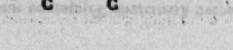
The residue of sodium salts of α- and β-hydroxy acids was decomposed with sulfuric acid, and the acids were extracted with ether. Ether was removed, and the acids were converted into their calcium salts. The water-insoluble calcium salts were filtered off and decomposed with sulfuric acid. The acids were extracted with ether and converted into ammonium salts, which were further converted into silver salts by reaction with silver nitrate solution.

Found %: Ag 43.13. $C_8H_{14}O_2Ag$. Calculated % Ag 42.9.

The silver content of the salt corresponded to a β-derivative of acrylic acid, which could be formed as the result of the decomposition of β-hydroxy acids containing eight carbon atoms. The structure of this acid was established by an examination of the products of its further oxidation, among which isobutyl methyl ketone and oxalic acid of m.p. 178-180° were isolated. Analysis of the acid of m.p. 178-180°:

Found %: C 23.30; H 4.25. $C_4O_4H_2$. Calculated % C 26.66; H 2.22.

The identification of 3,5-dimethyl-2-hexenoic acid



formed evidently from 3,5-dimethylhexanoic acid

indicates the presence of 4,6-dimethyl-1-heptene among the C_9 olefins.

Investigation of the volatile acids. The steam-distilled volatile acids were fractionated into 5° fractions. The fraction of b.p. 175-180° gave a white amorphous precipitate, which did not dissolve in the usual solvents and decomposed without melting at above 250°.

Found %: C 52.89; H 7.86; O 39.32. $C_3H_4O_2$. Calculated %: C 56.31; H 6.98; O 37.11.

The somewhat high values for hydrogen and oxygen indicate the presence of moisture. The presence of acrylic acid was proved by the reduction of silver nitrate and the preparation of a polymer of the acid, analysis of which gave the following results:

Found %: C 49.90; H 8.47. $C_3H_4O_2$. Calculated %: C 50 H 5.56.

Propionic acid was also identified (elementary analysis and silver salt).

Investigation of neutral oxidation products. The ketone fraction, b.p. 54-130°, was fractionated through a 40-plate column into 2° fractions. Semicarbazones were prepared from all these fractions. From the melting points and mixture melting points of the semicarbazones, the ketones shown in the table were identified.

Fraction (b.p. in °C)		Semicarbazone			
		N found (%)	N calculated (%)	M.p. (°C)	Data in literature
54-56	Acetone	—	—	188	188 [12]
78-80	Ethylmethyl ketone	—	—	145-146	146 [11]
92-94	Isopropyl methyl ketone	29.61	29.73	110-111	110 [12]
112-116	Mixture of isobutyl methyl ketone and	26.66	26.75	129-130	130 [12]
116-118	sec-butyl methyl ketone	—	—	110	—
122-128	Methyl neopenthyl ketone	24.35	24.56	176	176 [13]

The fractions of b.p. 112-116° and 116-118° were found to be mixtures of two ketones — isobutyl methyl and sec-butyl methyl ketones. For sec-butyl methyl ketone the 2,4-dinitrophenylhydrazone, m.p. 69-70° was prepared.

The formation of isobutyl methyl ketone and propionic acid indicate the presence of 4,6-dimethyl-3-heptene, the formation of ethyl methyl ketone — 3,4,5-trimethyl-3-hexene, the formation of ethyl methyl ketone and methyl propyl ketone — 3,4-dimethyl-3-heptene, etc. In addition, hydroxy ketones were isolated with the same number of carbon atoms as the original C_9 olefins; apart from the previously identified substance having a semicarbazone of m.p. 198°, an isomeric hydroxy ketone having a semicarbazone of m.p. 157° was isolated.

Found %: N 19.99. $C_{10}H_{21}O_2N_3$. Calculated %: 19.52.

When this hydroxy ketone was oxidized with periodic acid, the products were 2-methylbutyric acid and ethyl methyl ketone. The structure of the hydroxy ketone can therefore be considered to be:

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CO-\underset{\displaystyle CH_3}{\underset{|}{C(OH)}}-C_2H_5$$

SUMMARY

1. It was established that, unlike the polymerization of propene over phosphoric acid (which proceeds by simple stepwise addition of propene), its polymerization over zinc chloride is accompanied by isomeric changes which result in the formation of hydrocarbons containing quaternary carbon atoms.

2. It was shown that, apart from trialkylalkenes containing quaternary carbons or three consecutive tertiary carbons, the propene trimers included also dialkylalkenes (3,4-dimethyl-3-heptene, 2,6-dimethyl-2-heptene, and 4,6-dimethyl-1-heptene) and the monoalkylalkene 7-methyl-3-octene.

3. The formation of only slightly branched olefins indicates that in the polymerization of propene isomeric changes occur, not only in the direction of the formation of highly branched forms, but also in the reverse direction, with conversion of highly branched forms into only slightly branched forms according to the mechanism of isomeric transformations in the corresponding carbonium ions.

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BRIEF COMMUNICATIONS

PHYSICAL PROPERTIES OF cis-1,3,5-TRIMETHYLCYCLOHEXANE

A. L. Liberman, M. A. Pryanishnikova, and B. A. Kazansky

There are few data in the literature on the physical properties of cis-1,3,5-trimethylcyclohexane. The first preparations which, judging by their freezing points, may be identified with this stereoisomer were obtained by Eykman [1] in 1911, Eisenlohr [2] in 1925, and Leslie [3] in 1934. Later, in 1955, Chiurdoglu [4] made an attempt to separate a mixture of the stereoisomers of 1,3,5-trimethylcyclohexane by fractionation through a column. The physical properties of all these preparations of cis-1,3,5-trimethylcyclohexane – and also of the trans isomer [4], for comparison – are given in the table. Unfortunately, in none of the cited papers is there any indication of the degree of purity of the preparation. Although Chiurdoglu's preparation would appear to be the purest, our results show that even this was appreciably contaminated with the trans form, the boiling point of which is only 2° higher than that of the cis form. The constants published by this author therefore require some correction.

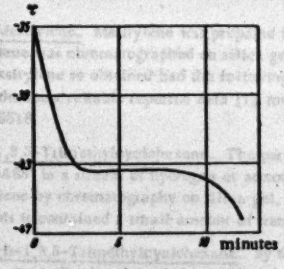

Fig. 1. Freezing curve of cis-1,3,5-trimethylcyclohexane

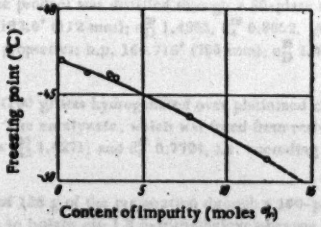

Fig. 2. Relation between freezing point of cis-1,3,5-trimethylcyclohexane and content of impurity.

Like all previous investigators, we prepared cis-1,3,5-trimethylcyclohexane by the hydrogenation of mesitylene, but we purified the mesitylene very carefully and we distilled the mixture of stereoisomers through a 100-plate column. The trans isomer, which was present in the mixture in small amount, was not isolated. The content of trans form in our preparation was established from the freezing curve (Fig. 1) and the cryoscopic constant, which, in its turn, was found from the depression of freezing point brought about by the addition of 1.7 moles % of methylcyclohexane.

Since refractive indices and specific volumes of hydrocarbons of a single class follow an additive law in mixtures, we were able to calculate the content of impurity (evidently trans isomer) in Chiurdoglu's preparation from these constants. For this calculation we used our data for the cis form and Chiurdoglu's data for the trans-

form. The same result was obtained both from refractive indices and from specific volumes: the preparation of cis-1,3,5-trimethylcyclohexane obtained by Chiurdoglu contained 12 moles % of impurity.

We prepared mixtures of our cis-1,3,5-trimethylcyclohexane with trans-1,3,5-trimethylcyclohexane, and one of these mixtures approximated to the above-mentioned mixture in content of impurity (12.4 moles %). The relation of the freezing point of cis-1,3,5-trimethylcyclohexane to the molar content of impurity is shown in Fig. 2. For Chiurdoglu's preparation, extrapolation gives a content of impurity of about 15%, which is fairly close to the value found from other constants.

TABLE

Constants of cis-1,3,5-Trimethylcyclohexane

Authors	B.p., °C	Freezing point (°C)	n_D^{20}	d_4^{20}
Eykman	136—137	—50	—	0.7744 (at 15.7°)
Eisenlohr	138—139	—	1.42710*	0.7720
Leslie	138.9	—50.7	1.4288 (at 25°)	—
Chiurdoglu	138.55	—50**	1.42680*	0.77050
Present authors	138.4	—43.2	1.4263	0.76942
Chiurdoglu for trans isomer	140.5	—107.5	1.43100*	0.77887

* For the yellow helium line.

** For the same preparation Timmermans [5] found freezing point −49.7°.

EXPERIMENTAL

Mesitylene. Mesitylene was prepared from acetone in the usual way [6]. In order to purify it, the crude mesitylene was chromatographed on silica gel and 300 g of the product was distilled through a 60-plate column. The mesitylene so obtained had the following constants: b.p. 103.0° (112 mm); n_D^{20} 1.4995; d_4^{20} 0.8652. According to the most reliable reported data [7], mesitylene has the properties: b.p. 164.716° (760 mm); n_D^{20} 1.49937; d_4^{20} 0.86518.

1,3,5-Trimethylcyclohexane. The purified mesitylene (160 g) was hydrogenated over platinized charcoal at 180–185° in a stream of hydrogen at atmospheric pressure. The catalyzate, which was freed from residual mesitylene by chromatography on silica gel, had the constants n_D^{20} 1.4271; and d_4^{20} 0.7724, i.e. according to its constants it contained a small amount of trans form.

cis-1,3,5-Trimethylcyclohexane. By the fractionation of 138 g of the preparation through a 100-plate column at a reflux number of about 150, it was found possible to isolate cis-1,3,5-trimethylcyclohexane giving a good freezing curve (Fig. 1). Judging from the freezing curve and the cryoscopic constant (0.0342 mole per mole per degree), the purity of our preparation was not less than 99.5 %. Its physical constants are given in table.

For the determination of the cryoscopic constant and the relation between the freezing point of 1,3,5-trimethylcyclohexane and the content of impurity, binary mixtures were prepared from this hydrocarbon and methylcyclohexane [b.p. 101.1° (760 mm); n_D^{20} 1.4230; d_4^{20} 0.7693] or trans-1,2-dimethylcyclohexane [b.p. 123.6° (760 mm); n_D^{20} 1.4270; d_4^{20} 0.7762]. The temperatures of incipient freezing of the mixtures are given in Fig. 2. The highest point (−43.05°) was found by calculation for zero content of impurity.

SUMMARY

1. cis-1,3,5-Trimethylcyclohexane was obtained in a higher state of purity than previously described preparations of this substance. Its physical constants are given.

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ORGANOBORON COMPOUNDS

COMMUNICATION 12. SYNTHESIS OF ARYLDICHLOROBORINES

B. M. Mikhailov and T. V. Kostroma

All the known methods of preparing aryldihaloborines depend on exchange reactions between organometallic compounds and boron halides. Aryldichloroborines were prepared by Michaelis and coworkers [1-4] by the action of boron trichloride on diarylmercury compounds. Apart from the need to use organomercury compounds, this method has the further disadvantage that it is generally necessary to heat the reactants in sealed tubes at 200° for a long time. In no case do the authors indicate yield.

Aryldibromoborines were prepared similarly [4]. Of the fluoro compounds, only difluorophenylborine has been described [5]; it was prepared by the action of diphenylzinc or boron trifluoride. It was not found possible to obtain this compound from boron trifluoride and phenylmagnesium bromide, since the reaction was so vigorous that all three fluorine atoms were replaced by organic radicals [6].

For the preparation of aryldichloroborines we made use of the reaction between areneboronic esters and phosphorus pentachloride. As we have shown [7], reaction between equimolecular amounts of areneboronic esters and phosphorus pentachloride gives arenechlorobronic esters $ArB\begin{matrix}Cl\\OR\end{matrix}$, in accordance with the equation:

$$ArB(OR)_2 + PCl_5 \rightarrow ArB\begin{matrix}Cl\\OR\end{matrix} + RCl + POCl_3.$$

We have now shown that the use of two equivalents of phosphorus pentachloride instead of one results in the replacement of both alkoxy groups of he areneboronic ester with formation of an aryldichloroborine in good yield:

$$ArB(OR)_2 + 2PCl_5 \rightarrow ArBCl_2 + 2RCl + 2POCl_3.$$

The reaction proceeds in two stages. The first equivalent of PCl_5 reacts with the areneboronic ester with spontaneous evolution of heat. In this stage PCl_5 is added at such a rate that the temperature of the reaction mixture remains at about 70-80°. When reaction is complete, alkyl halide and phosphoryl chloride are distilled off under reduced pressure, and a second equivalent of PCl_5 is added to the residue of crude arenechloroboronic ester. The second stage of the reaction

$$ArB\begin{matrix}Cl\\OC_6H_5\end{matrix} + PCl_5 \rightarrow ArBCl_2 + C_6H_5Cl + POCl_3$$

Ar = C_6H_5, o-$CH_3C_6H_4$, p-ClC_6H_4

is much slower than the first, so that it is necessary to heat the reaction mixture at 105-110° for several hours with continuous removal of the phosphoryl chloride and alkyl halide formed by vacuum distillation. In this way, from isobutyl esters of the appropriate acids we prepared dichlorophenyl-, dichloro-o-tolyl-, and dichloro-p-chlorophenyl-borines in about 60% yield.

We have prepared more arenechloroboronic esters [7]: isobutyl esters of p-chlorobenzene- and 1-naphthalene-chloroboronic acids were obtained in 76-80% yield by the action of PCl_5 (one equivalent) on p-chlorobenzene- and 1-naphthalene-boronic esters.

EXPERIMENTAL

Isobutyl p-chlorobenzenechloroboronate. A Claisen flask containing 26.9 g (0.1 mole) of diisobutyl p-chlorobenzeneboronate was shaken vigorously by hand while 20.8 g (0.1 mole) of finely ground phosphorus pentachloride was added in portions. Reaction began spontaneously and was accompanied by evolution of heat. The temperature was maintained at 60-70° during the addition. When the whole of the phosphorus pentachloride had reacted, isobutyl chloride and phosphoryl chloride were distilled from the reaction mixture into a receiver cooled with solid carbon dioxide. The residue was fractionally distilled and gave 18.6 g (80.5%) of isobutyl p-chlorobenzenechloroboronate, b.p. 121-123° (8 mm) and d_4^{20} 1.125.

Found %: B 4.75; Cl 15.67*. $C_{10}H_{12}BOCl_2$. Calculated %: B 4.76; Cl 15.35.

The product was a colorless liquid which readily hydrolyzed in the air. In addition, 11.2 g of phosphoryl chloride and 9 g of isobutyl chloride were obtained.

Isobutyl 1-naphthalenechloroboronate. The procedure was as in the previous experiment. Reaction between 56.8 g (0.2 mole) of diisobutyl 1-naphthaleneboronate and 41.7 g (0.2 mole) of phosphorus pentachloride gave 37.3 g (76%) of isobutyl 1-naphthalenechloroboronate, b.p. 167.5-169° (9 mm) and d_4^{20} 1.091.

Found %: B 4.50; Cl 14.45. $C_{14}H_{16}BOCl$. Calculated %: B 4.46; Cl 14.40.

The chloroboronic ester was a colorless liquid, readily hydrolyzed in the air.

Dichlorophenylborine. Phosphorus pentachloride (83.4 g, i.e., 0.4 mole) was added in portions to 46.8 g (0.2 mole) of diisobutyl benzeneboronate contained in a Claisen flask. Addition of the first equivalent of PCl_5, which was accompanied by evolution of heat, was made at such a rate that the temperature of the reaction mixture remained at about 70-80°. About one hour was required for this operation, and isobutyl chloride and phosphoryl chloride were then distilled off under reduced pressure. The second half (0.2 mole) of the phosphorus pentachloride was then added to the residue over a period of 3.5 hours at a temperature of 105-110°, so that isobutyl chloride and phosphoryl chloride were continuously distilled off in a stream of nitrogen into a receiver cooled with solid carbon dioxide. After the whole of the phosphorus pentachloride had reacted, the reaction mixture was fractionally distilled and gave 18.9 g (60%) of dichlorophenylborine, b.p. 73-75° (28 mm) (the literature [1] gives b.p. 175°).

Found %: B 6.91; Cl 44.29. $C_6H_5BCl_2$. Calculated %: B 6.91; Cl 44.65.

In addition, 18 g (97%) of isobutyl chloride and 27 g (88.8%) of phosphoryl chloride were obtained.

Dichloro-o-tolylborine. The procedure was as in the preceding experiment. Reaction was between 49.6 g (0.2 mole) of diisobutyl o-toluneboronate and 83.4 g (0.4 mole) of phosphorus pentachloride, and the product, amounting to 21.5 g (60.3%), was dichloro-o-tolylborine, b.p. 96-97° (28 mm) (the literature [1] gives b.p. 193°).

Found %: B 6.24; Cl 40.93. $C_7H_7BCl_2$. Calculated %: B 6.35; Cl 41.04.

Dichloro-p-chlorophenylborine. The procedure was as in the preceding experiments. Reaction between 53.7 g (0.2 mole) of diisobutyl p-chlorobenzeneboronate and 83.4 g (0.4 mole) of phosphorus pentachloride gave 23.9 g (62%) of dichloro-p-chlorophenylborine, b.p. 106-107° (24 mm).

Found %: B 5.59; Cl 36.63**. $C_6H_4BCl_3$. Calculated %: B 5.68; Cl 36.69.

* Boron-attached halogen was estimated.

** Readily hydrolyzed boron-attached halogen was determined.

The substance is readily hydrolyzed by atmospheric moisture.

SUMMARY

Aryldichloroborines were prepared in good yield by the action of two equivalents of phosphorus pentachloride on areneboronic esters.

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SYNTHESIS OF UNSATURATED ORGANOGERMANIUM COMPOUNDS

A. D. Petrov, V. F. Mironov, and I. E. Golgy

Like organosilicon compounds, organogermainum compounds can be prepared by direct synthesis, i.e. by direct reaction of an alkyl or aryl halide with elementary germanium at 300-350° in presence of a copper catalyst. In the direct synthesis use has been made of methyl chloride [1], ethyl chloride [2], propyl chloride [3], chlorobenzene [4], and methyl bromide [1].

In the case of ethyl and methyl chlorides, compounds of the type R_2GeCl_2 and $RGeCl_3$ are formed in a ratio of about 2:1. We repeated the direct synthesis of these compounds, but at much higher temperatures (about 550°). It was found that, under these conditions, the dialkyldichlorogermane content of the condensate was much lower. Dichlorodiethylgermane was not detected at all, and the yield of dichlorodimethylgermane was about the same as that of trichloromethylgermane. Also, for the first time, we made use of allyl and 2-methylallyl chlorides in the direct synthesis and so obtained good yields of the first representatives of unsaturated organogermainum compounds: allytrichlorogermane and trichloro (2-methylallyl)germane.

By reaction of Grignard reagents with alkyl- and alkenyl-chlorogermanes obtained in the direct synthesis, we synthesized some unsaturated tetrasubstituted germanes:

$$CH_2 = CHCH_2GeCl_3 + 3RMgX \rightarrow R_2GeCH_2CH = CH_2$$

$$CH_2 = \underset{\displaystyle CH_3}{\overset{|}{C}}CH_2GeCl_3 + 3CH_2MgCl \rightarrow (CH_2)_2GeCH_2\underset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$$

$$(CH_2)_nGeCl_{4-n} + (4-n)CH_2 = CHCH_2MgBr \rightarrow (CH_2)_nGe(CH_2CH = CH_2)_{4-n}$$

in which R = CH_3 and C_2H_5; n = 1 and 2.

We did not succeed in preparing trichlorovinylgermane by the direct synthesis; this compound was prepared by the chlorination of trichloroethylgermane and subsequent dehydrochlorination. Chlorination of trichloroethylgermane with sulfuryl chloride (which is widely used for the chlorination of organosilicon compounds [4]) went satisfactorily, and we obtained a 1:9 mixture of trichloro (1-chloroethyl)- and trichloro (2-chloroethyl)-germanes:

$$Cl_3GeCH_2CH_3 \xrightarrow{Bz_2O_2+SO_2Cl_2} Cl_3GeCHClCH_3 + Cl_3GeCH_2CH_2Cl.$$

In this connection it is interesting to note that, in the chlorination of trichloroethylsilane with sulfuryl chloride [5], trichloro (1-chloroethyl)- and trichloro (2-chloroethyl)-silanes are formed in the proportions of 1:2,5 [5]. The Cl_3Ge group therefore possesses a much greater orienting effect than the Cl_3Si group [4]. This effect is shown also in the fact that we were unable to bring about the chlorination of trichloromethylgermane with sulfuryl chloride in spite of the use of a fairly high temperature. It is interesting that chloromethylsilanes are also not chlorinated by sulfuryl chloride at low temperatures; however, this reaction does go at higher temperatures, even in the case of trichloromethylsilane [4].

The dehydrochlorination of trichloro (2-chloroethyl)germane with quinoline went satisfactorily with formation of trichlorovinylgermane in 26% yield:

$$Cl_3GeCH_2CH_2Cl \xrightarrow{\text{quinoline}} Cl_3GeCH{=}CH_2$$

With the object of making a comparative investigation of the unsaturated compounds of silicon, germanium, and tin, allyltrimethylstannane was prepared by the usual procedure:

$$(CH_3)_3SnBr + CH_2{=}CHCH_2MgBr \rightarrow (CH_3)_3SnCH_2CH{=}CH_2.$$

EXPERIMENTAL

Allyltrichlorogermane $CH_2 = CHCH_2GeCl_3$

Allyl chloride was passed through a glass tube, diameter 20 mm, filled with amixture of 25 g of finely divided germanium and 10 g of copper turnings and heated in an electric tube furnace to 340 ± 10°. The allyl chloride (300 g) was passed in at the rate of 60 drops per minute, and 170 g of condensate was collected. Distillation through a column gave 85 g of allyltrichlorogermane, b.p. 153.8° (743.5 mm); n_D^{20} 1.4928; d_4^{20} 1.5274.

The synthesis was carried out under similar conditions with 2-methylallyl chloride. The yield of trichloro-(2-methylallyl)germane, b.p. 42° (7 mm), was 35 g (24% on the condensate). Methyl and ethyl chlorides were passed at 550° at the rate of 60 bubbles per minute. In the case of methyl chloride the composition of the condensate was about 35% of trichloromethylgermane, b.p. 110° (727 mm), n_D^{20} 1.4685; and d_4^{20} 1.7053 and about 26% of dichlorodimethylgermane, b.p. 122° (727 mm), n_D^{20} 1.4600, and d_4^{20} 1.5053. In the case of ethyl chloride the condensate contained about 65% of trichloroethylgermane, b.p. 141° (760 mm); n_D^{20} 1.4750; d_4^{20} 1.6041.

Allyltrimethylgermane $CH_2 = CHCH_2Ge(CH_3)_3$

Allyltrichlorogermane (61 g) was gradually added to methylmagnesium chloride prepared from 22 g of magnesium in 400 ml of ether. The mixture was boiled for ten hours and then decomposed with water. The ether layer was separated from the aqueous layer, the aqueous layer was extracted with ether, and the combined ether extracts were dried with calcium chloride. Ether was removed, and distillation of the liquid residue through a column gave 30 g (68.1%) of allyltrimethylgermane, b.p. 101° (764 mm); n_D^{20} 1.4333; d_4^{20} 0.9952.

Found %: C 45.62; 45.69; H 9.03; 9.08; Ge 45.55; 45.70. $C_6H_{14}Ge$. Calculated %: C 45.38; H 8.88; Ge 45.72.

Diallyldimethylgermane $(CH_2 = CHCH_2)_2Ge(CH_3)_2$

An ethereal solution of dichlorodimethylgermane (31 g) was added to allylmagnesium bromide prepared from 6 g of magnesium with 24 g of allyl bromide in 400 ml of ether. The mixture was boiled for ten hours, and the usual treatment gave 14 g (42%) of diallyldimethylgermane, b.p. 146° (737 mm); n_D^{20} 1.4645; d_4^{20} 1.0337.

Found %: Ge 39.00; 39.61. $C_8H_{16}Ge$. Calculated %: Ge 39.28.

Triallylmethylgermane $(CH_2 = CHCH_2)_3GeCH_3$

Trichloromethylgermane (35 g) was added to allylmagnesium bromide prepared from 25 g of magnesium and 95 g of allyl bromide. The usual treatment gave 17 g (45%) of triallylmethylgermane, b.p. 190.5° (747 mm); n_D^{20} 1.4867; d_4^{20} 1.0222.

Found %: Ge 34.50; 34.34. $C_{10}H_{18}Ge$. Calculated %: Ge 34.43.

Allyltriethylgermane $CH_2 = CHCH_2Ge(C_2H_5)_3$

Trichloroallylgermane (23 g) was added to ethylmagnesium bromide prepared from 9 g of magnesium and 36 g of ethyl bromide in 200 ml of ether. The usual treatment gave 11 g (52.3%) of allyltriethylgermane, b.p. 50° (6 mm); 180° (732 mm); n_D^{20} 1.4594; d^{20} 1.0004.

Found %: C 53.25; 53.37; H 9.96; 10.026; Ge 35.73; 35.92. $C_9H_{20}Ge$. Calculated %: C 53.81; H 10.03 Ge 36.14.

Trimethyl(2-methylallyl)germane $CH_2=C(CH_3)-CH_2Ge(CH_3)_3$

Trichloro(2-methylallyl)germane (35 g) was added to methylmagnesium chloride prepared from 18.5 g of magnesium in 300 ml of ether. The usual treatment gave 11 g (42.5%) of trimethyl(2-methylallyl)germane, b.p. 121° (733 mm); n_D^{20} 1.4416; d_4^{20} 0.9908.

Found %: C 49.17; 49.17; H 9.52; 9.57. $C_7H_{16}Ge$. Calculated %: C 48.65; H 9.33.

Trichloro(1-chloroethyl)germane $CH_3ClCHGeCl_3$ **and Trichloro(2-chloroethyl)germane** $ClCH_2CH_2GeCl_3$

Freshly precipitated benzoyl peroxide (0.7 g) was added to a mixture of 100 g of trichloroethylgermane and 80 g of sulfuryl chloride. When the mixture was heated there was a vigorous evolution of gas, which stopped after two hours. Addition of a further 0.3 g of benzoyl peroxide caused further evolution of gas for a period of one hour. Distillation through a column gave 5 g of unchanged trichloroethylgermane; 5 g (4%) of trichloro(1-chloroethyl)-germane, b.p. 167° (746.5 mm), n_D^{20} 1.4948; and d_4^{20} 1.6975; and 44 g (38%) of trichloro(2-chloroethyl)germane, b.p. 188°(746.5 mm); n_D^{20} 1.5094. and d_4^{20} 1.7587.

Trichlorovinylgermane $CH_2=CHGeCl_3$

A mixture of 49 g of trichloro(2-chloroethyl)germane and 31 g of quinoline was distilled from a flask up to a temperature of 200°. Distillation of 35 g of the distillate through a column gave 4 g of germanium tetra-chloride, b.p. 83°, and 11 g (26.6%) of trichlorovinylgermane, b.p. 127.5° (745.5 mm); n_D^{20} 1.4816; d_4^{20} 1.6520.

Found %: C 11.40; 11.46; H 1.32; 1.36; Ge 34.73; 34.90; Cl 51.46; 51.12. $C_2H_3GeCl_3$. Calculated %: C 11.65; H 1.46; Ge 35.24; Cl 51.63.

Allyltrimethylstannane $CH_2=CHCH_2Sn(CH_3)_3$

Bromotrimethylstannane [6] (20 g) was added to allylmagnesium bromide prepared from 4 g of magnesium and 12 g of allyl bromide in 100 ml of ether. The mixture was boiled for ten hours, and the usual treatment and distillation through a column gave 8 g (47.6%) of allyltrimethylstannane, b.p. 125.5° (642 mm); n_D^{20} 1.4734; d_4^{20} 1.2549.

Found %: Sn 57.69; 57.95. C_6H_4Sn. Calculated %: Sn 57.93.

SUMMARY

1. The following organogermanium compounds containing unsaturated radicals were prepared for the first time: $CH_2=CHCH_2GeCl_3$; $CH_2=C(CH_3)CH_2GeCl_3$; $CH_2=CHGeCl_3$; $CH_2=CHCH_2Ge(CH_3)_3$; $CH_2=CHCH_2Ge(C_2H_5)_3$; $CH_2=C(CH_3)CH_2Ge(CH_3)_3$; $(CH_2=CHCH_2)_2Ge(CH_3)_2$; $(CH_2=CHCH_2)_3GeCH_3$.

2. It was shown that, in presence of benzoyl peroxide, sulfuryl chloride chlorinates trichloroethylgermane with formation of a 1:9 mixture of trichloro(1-chloroethyl)- and trichloro(2-chloroethyl)-germanes.

3. It was found that quinoline readily eliminates HCl from trichloro(2-chloroethyl)germane with formation of trichlorovinylgermane.

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PREPARATION OF CYCLOPENTENE FROM CYCLOPENTADIENE

A. F. Plate and V. I. Stanko

The usual laboratory method for the preparation of cyclopentene consists in the dehydration of cyclopentanol, which is prepared by the hydrogenation of cyclopentanone synthesized from adipic acid. The preparation of cyclopentene from cyclopentadiene by the action of calcium hexaammoniate was described by Kazansky and Glushnev [1]. David, Dupont, and Paquot [2] found an inflection on the curve for the hydrogenation of cyclopentadiene in alcoholic solution in presence of Raney nickel at room temperature and atmospheric pressure. When they interrupted the hydrogenation of cyclopentadiene after the adsorption of one molecular proportion of hydrogen, they were able to isolate a little cyclopentene. A patent [3] describes the formation of cyclopentene in 40% yield in the hydrogenation of cyclopentadiene at 430-470° in the presence of an $NiMoO_3$ catalyst at atmospheric pressure. Other investigators have also studied the hydrogenation of cyclopentadiene, but with the object of obtaining the ultimate hydrogenation product, cyclopentane [4-8].

TABLE

Experiments on the Hydrogenation of Cyclopentadiene (15 g of Raney nickel, initial pressure 70-80 atm, temperature about 20°).

Experiment	Amount of alcohol (ml)	Amount of cyclopentadiene (moles)	Hydrogen absorbed (moles)	Molar ratio of hydrogen absorbed to cyclopentadiene taken	Yield of cyclopentene (%)*
1	80	1.05	0.95	0.9 : 1	52
2	50	1.14	1.09	0.96 : 1	63
3	50	1.17	1.17	1 : 1	65
4	25	1.0	1.0	1 : 1	65
5	25	1.0	1.0	1 : 1	68
6	—	1.20	1.20	1 : 1	70
7	—	1.17	1.17	1 : 1	70

* Yield of cyclopentene isolated after fractionation through a 40-plate column.

With the object of establishing a preparative method, we carried out experiments on the hydrogenation of cyclopentadiene under pressure at room temperature in presence of Raney nickel, i.e. under the conditions for the preparation of cyclopentane [8], but with arrest of the process when one molecular proportion of hydrogen had been absorbed. In each experiment we took 66-88 g of cyclopentadiene and 15 g of catalyst. It was found that, under such conditions, the process went in a fairly selective fashion, and fractionation of the catalyzate through a column gave pure cyclopentene in yields of up to 70 % together with small amounts of unchanged cyclopentadiene (in the head fraction) and cyclopentane (in the residue from distillation). The results of some of the experiments are given in the table.

EXPERIMENTAL

Cyclopentadiene (b.p. 40-42°) was prepared by the depolymerization of technical dicyclopentadiene [fraction of b.p. 68-70° (19-20 mm)].

Catalyst was prepared from a 1:1 nickel-aluminum alloy, which was broken down into pieces of about 5 mm in size. One-half of the aluminum present in the alloy was leached out with alkali. All experiments were carried out over the same portion of catalyst; its activity was usually preserved until it broke down into a powder as a result of use.

Hydrogenation Experiments were carried out in a 250-ml stainless steel rotating autoclave. Catalyst (15 g), freshly distilled cyclopentadiene (66-80 g), and in some cases solvent were placed in the autoclave, hydrogen was blown through, and a pressure of 70-80 atm of hydrogen was then established in the autoclave. At first absorption of hydrogen was at the rate of 5-6 liters per hour, but owing to warming of the mixture by heat of reaction the rate of absorption increased after 20-25 minutes; after a second portion of hydrogen had been pumped in the rate of absorption attained 25-30 liters per hour. When the autoclave became hot, it was cooled to room temperature before the next charge of hydrogen. It was found that for an initial hydrogen pressure of below 50 atm there was no appreciable rise in temperature and hydrogen was absorbed at a rate of only 8-9 liters per hour.

After the absorption of 1 mole of hydrogen per mole of cyclopentadiene (it is convenient to use a manometer graduated in atmospheres), the autoclave was cooled with running water and excess of hydrogen was allowed to escape. The contents of the autoclave were removed, and the catalyst was washed with alcohol, the washings being added to the hydrogenation product. The catalyst was preserved under alcohol for use in the next experiment. The whole hydrogenation process generally occupied 1.75-2 hours. The reaction product was washed with water, dried with calcium chloride, and distilled through a 40-plate column filled with single turns of a nichrome spiral. The yield of cyclopentene are given in the table, its constants were b.p. 44.0° (760 mm), n_D^{20} 1.4222; d_4^{20} 0.7715. The literature [9] gives b.p. 44.2-44.4°, n_D^{20} 1.4228, and d_4^{20} 0.7713.

SUMMARY

A convenient laboratory method is proposed for the preparation of cyclopentene by the hydrogenation of cyclopentadiene. Yields of up to 70% are obtained.

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SYNTHESIS AND REACTIONS OF VINYL COMPOUNDS OF SILICON

COMMUNICATION 2. CATALYTIC VINYLATION OF HALO- AND ALKYLDIHALO-SILANES CONTAINING SILICON-ATTACHED HYDROGEN

M. F. Shostakovsky and D. A. Kochkin

We have previously shown that it is possible to vinylate alkyldihalosilanes containing silicon-attached hydrogen according to the reaction $CH \equiv CH + HSiR_3 \rightarrow CH_2 = CHSiR_3$, in which R may be halogen, alkyl, aryl, alkoxy, etc. [1]. In this way we prepared dichloromethyl- and dichloroethyl-vinylsilanes $CH_3CH_2 = CH)SiCl_2$ and $C_2H_5(CH_2 = CH)SiCl_2$. These substances were synthesized in an autoclave at a pressure of 20-30 atm by reaction between the alkyldichlorosilane and acetylene at 170-200°. Trichlorovinylsilane can be prepared also by direct synthesis, vinyl chloride being passed over a copper-silicon alloy at 350-400° [2]. The present paper describes a catalytic method for the preparation of trichlorovinylsilane, dichloromethylvinylsilane, and dichloroethylvinylsilane from the corresponding halosilanes and acetylene. The reaction was carried out in an electrically heated catalysis tube, a mixture of acetylene and halosilane being passed over a catalyst of palladium supported by alumina at 260-300°. Other catalysts can be used: platinum on alumina, on calcium or barium carbonate, or on silica gel, and palladium on the same carriers.

This method appears to be a new one: it is not described in the literature. It has the advantage that the reaction is carried out without the application of pressure, so that the synthesis is safe and is easily carried out on an industrial scale. The yields are higher: for all three products the catalytic method gives yields of 45-50%, whereas vinylation in an autoclave gives yields of 30-40%. The formation of the products can be represented as follows:

$$HSiCl_3 + CH \equiv CH \rightarrow CH_2 = CHSiCl_3 \quad (1)$$

$$RSiHCl_2 + CH \equiv CH \rightarrow R(CH_2 = CH)SiCl_2 \quad (2)$$

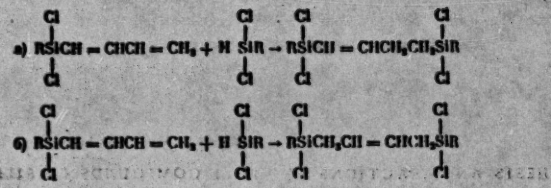
By-products are formed in the reaction as follows:

$$Cl_3SiCH = CH_2 + HSiCl_3 \rightarrow ClSiCH_2CH_2SiCl_3 \quad (3)$$

$$(Cl)_2RSiCH = CH_2 + HSiRCl_2 \rightarrow Cl_2RSiCH_2CH_2SiRCl_2 \quad (4)$$

Other compounds can also be formed in the course of the reaction:

$$\begin{matrix} Cl & & & & Cl \\ | & & & & | \\ RSiCH = CH_2 + CH \equiv CH \rightarrow R - SiCH = CHCH = CH_2 \\ | & & & & | \\ Cl & & & & Cl \end{matrix} \quad (5)$$



or (6)

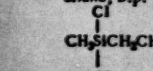
The apparatus used for the vinylation consisted of an electric muffle tube furnace, a stainless-steel catalysis tube, length 600-700 mm and diameter 18 mm, sulfuric acid and calcium chloride drying vessels, receiver, and reflux condenser attached to a trap cooled with solid carbon dioxide and acetone. Fractionation of the reaction products was carried out in a fractionation column 150 mm in height with a metal filling (20 theoretical plates).

EXPERIMENTAL*

1. Preparation of Catalyst (Palladium on Alumina). Alumina (13 g in the form of 3 mm × 3 mm cylinders) was impregnated with an aqueous solution of 0.18 g of palladium chloride. The palladium chloride solution was evaporated to dryness on the alumina with constant stirring in a porcelain dish. The material was then transferred to the reaction tube and heated in a stream of hydrogen at 260-300° for 3-4 hours. The palladium chloride was then reduced to metallic palladium. Before being passed into the tube, the hydrogen was dried with calcium chloride and sulfuric acid. Catalyst prepared in this way contained 0.8% of palladium.

2. Preparation of trichlorovinylsilane by the vinylation of trichlorosilane. A gaseous mixture of trichlorosilane [b.p. 31-33° (756 mm); Cl content 78.42%] and acetylene was passed at 260-300° through the reaction tube in which the catalyst was spread over the whole length of the tube. The acetylene was first dried by passage over calcium chloride. The mixing of acetylene and trichlorosilane was effected in a graduated Tishchenko vessel containing trichlorosilane. Acetylene passed through the vessel picked up the required amount of trichlorosilane, which was passed into the reaction tube at 20-25 ml/hour. The extent to which the acetylene reacted was determined by the rate at which it left the vinylation apparatus. In the course of three hours, 60 g of condensate was obtained. Fractionation and analysis showed that the reaction products included 1) 25.2 g (42% on weight of condensate) of unchanged trichlorosilane, b.p. 32-35° (756 mm); 2) 21.3 g (35.5% on weight of condensate and 51.3% yield on the amount of trichlorosilane that reacted) of trichlorovinylsilane, b.p. 92° (742 mm), n_D 1.4350; and d_4^{20} 1.2650; 3) 5.8 g (9.8% on weight of condensate) of 1,1,1,4,4,4-hexachloro-1,4-disilabutane $Cl_3SiCH_2CH_2SiCl_3$, b.p. 200.5° (748 mm); and 4) 6.9 g (11% on weight of condensate) of high-boiling products.

3. Preparation of dichloromethylvinylsilane by the vinylation of dichloromethylsilane. A mixture of dichloromethylsilane (b.p. 41.0-43.0°, d_4 1.1047) and acetylene was passed through a tube containing the same catalyst at 260-280° for three hours; 70 g of dichloromethylsilane was passed and 65.0 g of condensate was collected. Fractionation of the reaction products through a column gave 1) 24.0 g (40% on weight of condensate) of dichloromethylsilane; 2) 24.3 g (45% yield on the amount of dichloromethylsilane that reacted) of dichloromethylvinylsilane, b.p. 91° (742 mm), n_D^{20} 1.4270 and d_4^{20} 1.0868; 3) 6.3 g of 2,2,5,5-tetrachloro-2,5-disilahexane



, b.p. 72-73.0°, n_D^{20} 1.4760, and d_4^{20} 1.2628; 4) 9.3 g of high-boiling products.

4. Preparation of dichloroethylvinylsilane by the vinylation of dichloroethylsilane. Acetylene was passed into the tube containing alumina-supported palladium from a cylinder, and 84.5 g of dichloroethylsilane (b.p. 74.5-76.0° (756.0 mm), n_D^{20} 1.4129, and d_4^{20} 1.0849) was added from a graduated buret through a side tube; reaction was at 260-270° for 4.5 hours. Fractionation of the 75.0 g of condensate gave 1) 35.0 g (46.6% on the weight of condensate) of unchanged dichloroethylsilane; 2) 20.7 g (34.8%) of dichloroethylvinylsilane, b.p. 118.5-119.5° (756 mm), n_D^{20} 1.4385, and d_4^{20} 1.0664); 3) 3.5 g (4.7% on the weight of condensate) of 3,3,6,6-tetrachloro-3,6-disilaoctane, b.p. 100-102° (8 mm), n_D^{20} 1.4790; and d_4^{20} 1.187; 4) 13.0 g (17.2% on the weight of condensate) of high-boiling products.

* V. V. Vinogradova, a student of Irkutsk State University, took part in the experimental work.

We consider that this method will be applicable to the vinylation of aryldihalosilanes.

SUMMARY

1. It was shown that halo- and alkyldihalo-silanes containing silicon-attached hydrogen (trichlorosilanes, dichloromethylsilane, and dichloroethylsilane) can be vinylated by passing them together with acetylene through a catalysis tube at 260-300°.

2. This method does not require the application of pressure and is technically simple.

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* T.p = C. B. Translation pagination.

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ROLE OF HYDROGEN DISULFIDE IN THE VULCANIZATION PROCESS

E. I. Tinyakova, E. K. Khrennikova, and B. A. Dolgoplosk

In a previous investigation [1] we have shown that many vulcanization accelerators, including ethylenediamine and its derivatives, ethanolamines, and hydroxy carbonyl compounds, react with sulfur at the vulcanization temperature with formation of hydrogen sulfide as main product. On anlogy with many oxidation-reduction systems in which oxygen takes part and reacts through the stage of hydrogen peroxide, the reaction of sulfur with vulcanization accelerators can be regarded as follows:

in which DH_2 is the vulcanization accelerator.

The species responsible for the initiation of the vulcanization process are ·SH radicals formed by the breakdown of hydrogen disulfide or hydrogen polysulfide. The breakdown of hydrogen disulfide in rubber solution at 50-70° results in the transformation of the rubber into a gel [1]. Its breakdown in paraffins and aromatic hydrocarbons leads to quantitative separation of hydrogen sulfide and sulfur [1,2]. We have shown that in the breakdown of hydrogen disulfide in α-olefins (styrene, α-methylstyrene, 1-pentene, and isoprene), which act as acceptors for free radicals, reaction proceeds at 50-70° without formation of hydrogen sulfide and sulfur, but with formation of addition products (mono-, di-, and tetra-sulfides).

The suppression of the reaction leading to evolution of hydrogen sulfide is associated with trapping of the intermediate breakdown product (the ·SH radical) by unsaturated compounds. Similar effects are observed when sulfur reacts with monoethanolamine in 1-pentene or α-methylstyrene solution at 130°. In ethylbenzene solution this reaction leads to the evolution of 80% of the theoretical amount of hydrogen sulfide. In the α-olefins, only addition occurs without formation of hydrogen sulfide. The table gives the compositions of products obtained by reaction of hydrogen disulfide with 1-pentene and of sulfur with monoethanolamine in presence of 1-pentene.

The formation of mono- and poly-sulfides is associated only with the formation of active intermediate products of the breakdown of hydrogen disulfide, for hydrogen sulfide does not add to the double bond in absence of free radicals. The formation of the products indicated can be explained on the assumption that HS· and HS_2· radicals take part in the initiation and development of the process.

EXPERIMENTAL

Hydrogen disulfide, b.p. 75°, was prepared by fractional distillation of hydrogen polysulfide [3]. 1-Pentene was prepared from ethyl bromide and allyl chloride [4]; it had b.p. 30°, n_D^{20} 1.3720; and d_4^{20} 0.6589. Isoprene, styrene, and α-methylstyrene were freed from stabilizer by shaking them with sodium hydroxide solution, after which they were washed with water, dried, and distilled.

The reactions were carried out in sealed tubes in a nitrogen atmosphere. At the end of the period of heating the tubes were cooled to −78° and H_2S was removed. The completeness of the decomposition of H_2S_2 was determined by shaking with $CdCl_2$ solution: absence of a precipitate of CdS_2 indicated complete decomposition of

TABLE

Compositions of the Products of the Reaction of 1-Pentene with Hydrogen Disulfide and with Sulfur and Monoethanolamine*

Fraction	Identity of fraction	B.p. in °C (p in mm)	d_4^{15}	n_D^{15}	Molecular weight	Elementary composition (%)			Yield of fraction (%)
						C	H	S	
Hydrogen disulfide + 1-pentene; 15 hours, 50°; concentration of H_2S_2 in pentene: 0.925 mole/liter									
I	Dipentyl sulfide	86—87 (12—13)	0.8446 (0.8439)	1.4572 (1.4584)	174 (174)	68.44 (68.96)	12.72 (12.64)	18.37 (18.39)	62
II	Dipentyl disulfide	68—75 (1)	0.9381		201 (206)	58.2 (58.25)	10.58 (10.68)	30.44 (31.07)	12.1
III		76—96 (1)				56.28	10.48	33.84	
IV	Dipentyl tetrasulfide	100—107 (1)	d_4^{20} 1.0134	n_D^{20} 1.5280	268 (270)	47.25 (44.44)	8.92 (8.15)	43.84 (47.40)	22.0
Sulfur + monoethanolamine + 1-pentene; 10 hours, 130°; concentration of S: 0.89 mole/liter; concentration of monoethanolamine: 1.0 mole/liter									
I	Dipentyl sulfide	86—90 (12)	0.8437	1.4568	170	68.66	11.54	19.47	28.6
II	Dipentyl disulfide	120—125 (12—13)	0.9310	n_D^{20} 1.5001	208	62.17	9.97	27.95	30.0

* Data from literature and calculated molecular weights and compositions are given in parentheses.

H_2S_2. In the solution, after treatment in this way, the mercaptan content and the total amount of elementary and polysulfide sulfur were determined [5]. 1-Pentene was distilled off, and the residue was vacuum-fractionated.

SUMMARY

It was shown that the breakdown of hydrogen disulfide in α-olefins results in the exclusive formation of addition products (mono-, di-, and tetra-sulfides) without formation of hydrogen sulfide and free sulfur. Similar results were obtained when sulfur reacted with monoethanolamine (vulcanization accelerator) in α-olefin solution.

The reaction products were isolated and characterized.

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CURRENT EVENTS

SECOND JOINT SCIENTIFIC SESSION OF THE CHEMICAL INSTITUTES OF THE TRANSCAUCASIAN ACADEMIES OF SCIENCES

A little more than two years ago, the First Joint Scientific Session of the Chemical Institutes of the Georgian, Azerbaidzhanian, and Armenian Academies of Sciences was held in Tbilisi. This session resolved to hold sessions of this sort systematically and to hold the next session in Baku.

The Second Joint Session took place on April 23-27 in the capital of Soviet Azerbaidzhan, Baku. It was opened by the president of the Azerbaidzhanian Academy of Sciences M. M. Aliev, who praised the initiative of chemists in calling joint scientific sessions, which would help to establish closer scientific relations between chemical and industrial workers. He expressed the hope that the work of the session would be fruitful.

The nineteen papers read at the session were devoted to current chemical problems closely associated with the demands of the national economy. Most of the papers contained new and important data relating to the chemical characteristics and possible utilization of the natural resources of the three Transcaucasian republics.

Much attention was attracted by the paper of the delegate to the Twentieth Congress of Communist Party of the Soviet Union Yu. G. Mamedaliev, academician of the Azerbaizhdanian Academy of Sciences. He discussed immediate tasks in the development of the petrochemical industry in the light of the resolutions of the Twentieth Congress of the Communist Party. The speaker drew attention to promising future prospects in the development of the manufacture of such important products as fertilizers, toxic substances, synthetic alcohol, detergents, synthetic fibers, etc. on the basis of petroleum.

Several papers were devoted to adsorption and catalysis (Yu. G. Mamedaliev, M. A. Dalin, A. Z. Shikhmamedbekova, T. I. Mamedov, Z. G. Zulfugarov, G. V. Krmoyan, G. I. Mikaelyan, Kh. I. Areshidze, and G. V. Tsitsishvili); new data were presented on the characteristics of various catalysts and adsorbents for several adsorption and catalytic processes of great practical importance. The papers by A. T. Babayan, B. K. Zeinalov, R. M. Lagidze, Sh. M. Mamedov, and L. D. Melikadze discussed the splitting of quaternary ammonium compounds, the complex utilization of the products in the paraffinous distillate, the alkylation of benzene with acetic esters, the synthesis and reactions of α-halo esters, and the nature of the petroleum aromatics of high molecular weight. Papers on the structure-mechanical properties and utilization of clay suspensions in oil-drilling were given by A. K. Miskarli, A. M. Gasparyan and A. P. Zaminyan, M. M. Gurvich, and L. A. Abduragimova. Papers by I. L. Bagbanly and E. M. Nanobashvili were concerned with various questions of chemical analysis and the geochemistry of copper, gallium, and germanium. The papers by M. V. Darbinyan and M. Nalchadzhanyan concerned the utilization of magnesia raw material and the mechanism of the corroding of electrodes in the electro-melting of glass.

The papers prompted lively discussions, in which the chemists of Azerbaidzhan took an active part. Hopes were expressed for the further development of various theoretical investigations and the application of the results of some of the investigations in industry. The speakers were unanimous in their praise of the excellent organization of the session under the guidance of the Azerbaidzhanian Academy of Sciences and the Institute of Chemistry of the Azerbaidzhanian Academy of Sciences.

The results of the session were summarized by the director of the Institute of Chemistry of the Azerbaidzhan Academy of Sciences, G. Kh. Efendiev. He pointed out that the session had made possible an exchange of experience and the further strengthening of the creative bond between Transcaucasian chemists. At the same time the lines along which joint work should proceed in future were laid down. The session approved of the papers

presented and took note of the fact that the Institutes of Chemistry of the Academies of Sciences of the three Transcaucasian republics are carrying out work in fields of immediate importance in chemistry associated with the demands of the national economy. It was resolved that the questions for joint work should be recorded and the transactions of the session should be published. The next session is to be in Erevan in 1957.

The participants in the session made themselves acquainted with the work of various scientific establishments and industrial concerns and with the noteworthy sights of the city of Baku.

Salutation to Semen Isaakovich Volfkovich

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences congratulate you on the attainment of the age of sixty years and the completion of thirty-five years of varied activities in science, teaching, and the organization of scientific work.

Your investigations on the chemistry and technology of phosphorus, phosphoric acid and its salts, and nitrogen, potassium, and fluorine compounds are widely known among chemists.

We wish you good health, continued creative activity, and further successes in all the fields in which you work.

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GENERAL AND INORGANIC CHEMISTRY

"COMPLEX" REDUCTION OF MULTIMETAL IRON AND NICKEL ORES AS A BASIS FOR NEW METHODS FOR THEIR CHEMICAL TREATMENT

G. G. Urazov and D. P. Bogatsky

In order to provide industry with a broader basis of ores and other raw materials and to effect "complex" utilization of raw materials (i.e., rational, simultaneous utilization of all useful components)– as required by the directives of the Twentieth Congress of the Communist Party of the Soviet Union– Soviet chemistry must solve some very important problems, the solution of which will contribute to the progress of chemical technology. Among these problems, the study of new sources of raw material and the development of new methods for their rational utilization are of primary importance. Accordingly, for some years we have been investigating the problem of the efficient utilization of low-grade complex multimetal iron and nickel ores by methods in which chemical treatments follow "complex" direct reduction. The problem of developing new chemical treatments must be solved in such a way that it is possible to extract not only iron, but also nickel, cobalt, chromium, vanadium, etc., in the form of finished products from these ores. As we have shown, such "complex" methods are provided by hydrometallurgical and chlorine-gas treatments, by means of which all the above-mentioned metals can be extracted from the reduced ores.

Processes of selective reduction of iron from its oxides and ores have been investigated in fair detail. Considerably less study has been devoted to the reduction of the other metals that can be extracted from complex iron ores. We have made a detailed study of the behavior of nickel in the direct reduction of low-grade and waste complex iron and nickel ores under various conditions.

The complex iron-nickel ores of the Urals contain nickel in the form of oxide, oxide-silicate, and sulfide minerals. The nickel oxide minerals (bunsenite, texasite, etc.), which are various non-siliceous nickelous compounds, exist in the complex ores mainly in the "impregnation" state and contain a rather small part of the total amount of nickel present. In complex iron ores most of the nickel is present as oxide-silicate minerals, which are magnesium-nickel and magnesium-iron-nickel hydrosilicates and hydroaluminosilicates of variable composition and having a metacolloidal character; they are mineral gels, i.e., ultimate products of all normal weathering of peridotites and serpentinites that have not undergone previous transformations and have not been subjected to a thermal treatment. They include garnierite (Ni, Mg)O·SiO_2·H_2O, which contains up to 45% of nickelous oxide; nepouite-revdinskite-3 (Ni, Mg)O·$2SiO_2$·$2H_2O$, which contains about the same amount of nickelous oxide; nickel cerolite (Mg, Ni)O·SiO_2·H_2O which contains up to 1% of nickelous oxide; nickel deweylite-4 (Mg, Ni)O·$3SiO_2$·$3H_2O$, which contains up to 5% of nickelous oxide; nickel aluminosilicate; and aidyrlite, the chemical formula of which has not yet been determined – it contains up to 32% of nickelous oxide. Nickel is found in complex iron ores not only in these silicate minerals, but also, in the impregnation state, in nontronite $0.5RO(Al, Fe)_2O_3 \cdot 8SiO_2 \cdot 3H_2O$, in which RO = MgO, CaO, and NiO, the nickelous oxide content being 3–5%, and in serpentine $3MgO \cdot 2SiO_2 \cdot 2H_2O$, which contains up to 1% of adsorbed nickelous oxide. Nickel frequently occurs also in asbolan $MnO \cdot MnO_2 \cdot nH_2O + CoO + NiO$, which may contain up to 10-12% of nickelous oxide in the impregnation state.

Magnesium nickel hydrosilicates and aluminosilicates of variable composition, and also hydrated nickelous oxide and other non-siliceous nickel compounds are by no means invariably present in complex iron ores in a clearly individualized form. Most frequently, they are finely dispersed through the whole mass of these ores and very frequently permeate the various mineral ingredients of the gangue, which contains, in particular, quartz, chalcedony, opal, and other mineralogical modifications of silica. In accordance with the form in which nickel occurs (mainly in the oxide state in all ores which contain iron and cobalt), D. P. Bogatsky classifies complex iron-nickel ores as follows: 1) oxide ores, in which nickel is present mainly as hydrated nickelous oxide, sulfate,

and other mainly nonsiliceous oxide minerals, and in which iron and cobalt are present as oxides; 2) oxide-silicate ores, in which nickel is present mainly as magnesium nickel hydrosilicates and hydroaluminosilicates of variable composition but partly as nonsiliceous oxide minerals, and in which iron and cobalt are present mainly as oxides; 3) oxide-sulfide-silicate minerals, which contain iron and nickel as silicate and oxide compounds, and also as sulfides.

EXPERIMENTAL

Physicochemical investigations that we carried out on ten different complex iron ores showed that iron, nickel, and cobalt were present as oxides and silicates and that it is desirable and, in principle, possible to employ the process of complex direct reduction as a general technological basis for the extraction of all iron–group metals from these ores. In order to determine the optimum conditions for carrying out this process in practice, experimental and theoretical studies were made of largely uninvestigated processes of calcination and direct reduction of oxide and silicate nickel compounds and minerals, and also of the reduction of iron-nickel ores with hydrogen, carbon monoxide, a mixture of carbon monoxide and dioxide, and carbon.

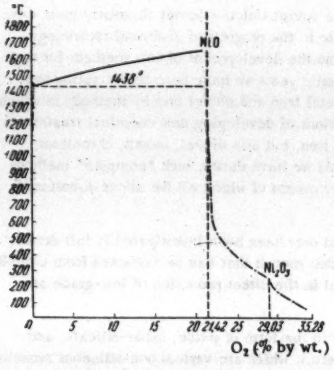


Fig. 1. Phase diagram of the nickel-oxygen system (Bogatsky).

An investigation of the phase diagram of the nickel-oxygen system (Fig. 1), carried out with the object of identifying the forms in which nonsiliceous nickel compounds may be present in complex iron ores, showed that nickelous oxide, nickelic oxide, and nickel dioxide occur together with continuous series of solid solutions between these. An experimental and theoretical study of the dissociation of these oxides and their solid solutions at high temperatures provided an explanation for the results of a study of the rational chemicometallurgical composition of the nonsiliceous nickel compounds in complex iron ores. It was established that, at the very beginning of the process of calcination in the course of direct reduction under practical conditions, together with removal of adsorbed and constitutional water of crystallization, dehydration of nonsiliceous nickel oxide minerals occurs. These processes together with the inevitable dissociation processes occurring in oxides other than nickelous oxide and in nonsiliceous nickel compounds, if they are present in the ore, finally result in the formation of only nickelous oxide, or its solid solutions with nickelic oxide. Hence, at the temperatures required for rapid direct reduction, of the various nickel minerals in complex oxide-silicate iron ores the following partially or wholly dehydrated minerals react: nickelous oxide and its solid solutions with nickelic oxide, and also magnesium-nickel and magnesium-iron-nickel silicates and aluminosilicates, the reduction of which was submitted to investigation.

The main results of our experimental and theoretical investigations of direct-reduction processes on these nickel-containing components of complex iron ores are given briefly below. Experimental investigations of the equilibrium in the reaction of reduction of nickelous oxide with hydrogen showed that the equilibrium constant for this reaction $K_p = P_{H_2O} : P_{H_2}$ varies from 15.2 at 450° to 75.9 at 1000° in accordance with the equation $\log K_p = -\frac{1169}{T} + 2.803$ (Fig. 2). Experimental investigation of the equilibrium in the reduction of nickelous oxide with carbon monoxide showed that the equilibrium constant for this reaction $K'_p = P_{CO_2} : P_{CO}$ varies from 554.6 at 500° to 57.2 at 1100° in accordance with the equation $\log K'_p = \frac{1735.1}{T} + 0.49935$ (Figures 3 and 4), which has been confirmed by other authors.

The temperature at which reduction of nickelous oxide by hydrogen begins to become appreciable is about 229-230°, and for reduction with carbon monoxide it is about 344-346°. Complete reduction of nickelous oxide with hydrogen is attained at 700° in three hours and at 800° in one hour (Fig. 5). At 900°, complete reduction of nickelous oxide is attained in one hour (Fig. 6). Solid solutions of nickel oxides begin to be reduced

at lower temperatures - depending on their compositions. For the solid solution of nickel oxides obtained by calcination of the nitrate to constant weight in air at 600°, reduction by hydrogen begins at about 111-112°, complete reduction being complete in two hours at 700°. The temperature at which the same solid solution begins to be reduced by carbon monoxide is about 120-122°, and complete reduction is attained in one hour at 900°.

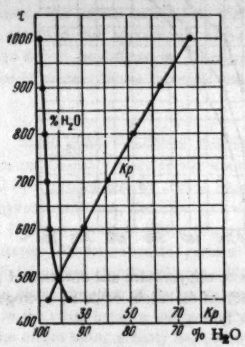


Fig. 2. Temperature-dependence of equilibrium in the reaction $NiO + H_2 = Ni + H_2O$ (Bogatsky).

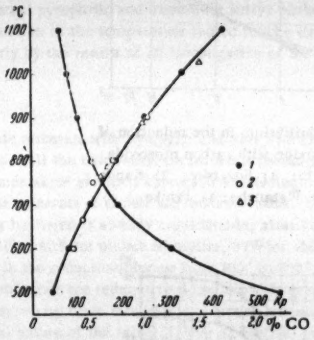


Fig. 3. Temperature-dependence of equilibrium in the reaction $NiO + CO = Ni + CO_2$; 1) Bogatsky, 1935; 2) Smirnov, 1941; 3) Fricke and Weitbrecht, 1942.

On the basis of the experimental equilibrium data, thermodynamic investigations were carried out. These yielded the following: equations for the temperature-dependence of enthalpy and free energy changes for the reversible reactions of reduction of nickelous oxide by carbon monoxide:

$$\Delta H = -46\,000T^{-1} - 9.21T + 0.0_2492T^2 - 0.0_6627^3 + 12\,293:$$

$$\Delta F = 12\,293 - 23\,000T^{-1} + 21.21T\log T - 61.29T - 0.0_2492\,T^2 + 0.0_6317T^3:$$

and of reduction of nickelous oxide by hydrogen:

$$\Delta F = \frac{23\,000}{T} + 60.75T - 25.38T\log T + 0.0_2937T^2 - 0.0_699T^3 - 2193:$$

the heats of reaction and free energy changes for these reactions under standard conditions; the equation for the temperature-dependence of the free energy of the dissociation reaction (formation of nickelous oxide):

$$\Delta F = 23000T^{-1} - 27.54T\log T + 56.83T + 0.0_3772T^2 - 0.0_6627^3 + 55217:$$

the temperature-dependence of the dissociation pressure of nickelous oxide (Fig. 7); the heat of reaction ($\Delta H^\circ_{298.1} = -58285$ cal) and free energy change ($\Delta F^\circ_{298.1} = -52,591$ cal)for the formation of nickelous oxide, and its entropy under standard conditions ($S^\circ_{298.1} = 8.01$ cal/degree).

These experimental and theoretical investigations showed that nickelous oxide and its solid solutions are very readily reduced, so that previously dehydrated and calcined non-siliceous oxide minerals in complex iron ores are reduced considerably more readily than ferrous and ferrous-ferric oxides, but somewhat less readily than ferric oxide. The heat of the reduction of nickelous oxide with hydrogen is negative, but is extremely small. The heat of the reduction of nickelous oxide with carbon monoxide has a high positive value, i.e., this reaction is exothermic, like the reduction of ferric oxide with hydrogen or carbon monoxide at high temperatures. This fact is of great technological importance for the simplification of the comple direct reduction of iron ores under practical conditions.

Investigation of the reduction of nickelous oxide with carbon showed that the process is highly endothermic and can be detected thermographically from temperatures of about 585-600° and upwards. Almost complete reduction

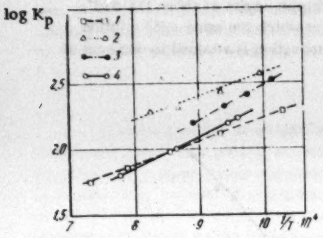


Fig. 4. Equilibrium in the reduction of nickelous oxide with carbon monoxide according to: 1) Bogatsky; 2) Kapustinsky; 3) Watanabe; 4) Fricke.

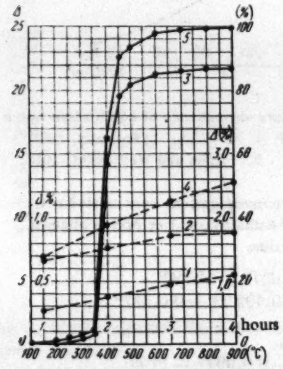


Fig. 6. Effect of temperature and duration of process on the reduction of nickel oxides by carbon monoxide:
1) reduction of solid solution of nickel oxides at 200° for 1, 2, 3, and 4 hours; 2) reduction of solid solution of nickel oxides at 300° for 1, 2, 3, and 4 hours; 3) temperature-dependence of the reduction of solid solution of nickel oxides for one hour; 4) reduction of nickelous oxide at 300° for 1, 2, 3, and 4 hours; 5) temperature-dependence of the reduction of nickelous oxide for one hour.

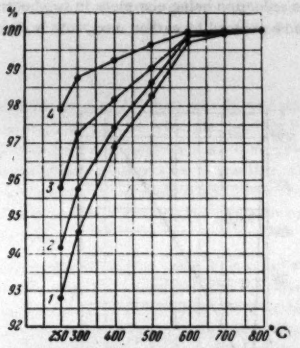
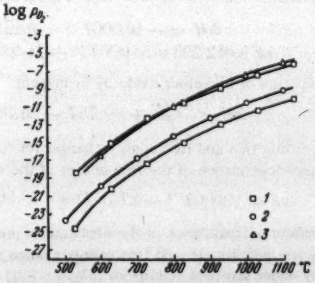


Fig. 5. Effect of temperature and duration of process on the reduction of nickelous oxide by hydrogen (1, 2, 3, and 4 hours).



7. Temperature-dependence of the dissociation equilibrium in the formation of nickelous oxide according to 1) Kapustinsky; 2) Bogatsky; 3) Watanabe.

of nickelous oxide is effected by carbon at about 950-1000°. The reduction of nickelous oxide to nickel in complex iron ores is, from the practical point of view, much less rational when carried out with carbon, rather than with gaseous reducing agents:

1) the process is completed in the temperature region in which iron undergoes rapid carburization with formation of austenite, so that spongy formations greatly contaminated with carbon are formed together with other undesirable impurities; 2) under these conditions, the reduction of nickelous oxide, like that of iron oxides, is highly endothermic, so that its practical realization is greatly complicated; 3) the reduced nickel (and also ferronickel) is considerably less active chemically than the more finely dispersed pyrophoric and extremely active nickel (ferronickel) obtained with appreciable cementation by gaseous reduction in the temperature region for the existence of iron in the α-modification. This was confirmed very clearly by the results of an investigation of the reduction processes of oxide-silicate minerals and complex iron ores.

Under given conditions, the reduction of oxide-silicate minerals with hydrogen and also with CO proceeds considerably more slowly than that of nickelous oxide. All the oxide-silicate minerals investigated are reduced by hydrogen and by carbon monoxide at below the temperature at which appreciable sintering occurs. Under given conditions, the extent to which the various silicate minerals of nickel are reduced varies. In one hour at 600,° the extent to which these minerals are reduced by hydrogen is already considerable, attaining 25-45% for garnierite, 61% for nepouite-garnierite, 32% for nickel cerolite, 42% for nickel deweylite, 37% for aidyrlite, and 55% for nickel aluminosilicate. With rise in temperature in the reduction process from 600° to 800° and with increase of the duration of the process to four hours, all these minerals are reduced to a considerably greater extent. On the other hand, a substantially different behavior is shown by these minerals in reduction processes at 900°, the effect being greatly dependent on the physiochemical nature of the mineral. For garnierite, nepouite-garnierite, and aidyrlite at 900°, the extent of reduction increases with increase in the duration of the reduction process, but the extent of reduction of nickel deweylite and cerolite at 900° diminishes appreciably as the duration of the reduction process is increased. This is to be explained by the effect of crystallization or recalescence (established thermographically), which occurs when these and similar magnesial silicates are heated at 800-900° In this temperature region the thermograms of deweylite, cerolite, and associated minerals of this class show considerable exothermic effects (Figures 8 and 9) which, according to x-ray investigation, is due to the crystallization or recalescence of a mineralogical component of the olivine type. The evolution of heat is due to appreciable increase in the grain size of the mineral, i.e., to the conversion of the substance from the amorphous or finely crystalline state into a more coarsely crystalline state, a change that is associated with a corresponding reduction in free energy and increase in entropy of the system.

In order to avoid the undesirable effects of this process on the extraction of the reduced metal, it is necessary and sufficient first to calcine the mineral at temperatures above the temperature established thermographically for the beginning of the exothermic crystallization effect; grinding and reduction may then follow. Hence, differential thermographic investigation of the physicochemical nature of silicate minerals indicates practical methods for improving the extraction of reduced metal from them. For those oxide-silicate minerals which give a crystallization effect in the differential thermographic investigation, almost complete extraction of nickel should be attained either a) by reduction of the minerals below the temperature of the crystallization effect, the other conditions of the reduction process being made as favorable as possible, or b) by reduction of these minerals after prior calcination at a temperature of not lower than the characteristic temperature for the beginning of the crystallization effect in the particular mineral. Complete reduction of oxide-silicate minerals is attained under the following conditions:

	Reduced with Hydrogen	Reduced with Carbon Monoxide
a) Garnierite	at 900° for 4 hr	
b) Nepouite-garnierite	at 800° for 3 hr	at 800° for 3 hr
c) Cerolite *	at 900° for 1 hr	at 900° for 2 hr
d) Deweylite *	at 900° for 0.5 hr	at 900° for 0.5 hr
e) Aidyrlite	at 900° for 0.5 hr	at 900° for 2 hr
f) Aluminosilicate	at 800° for 3 hr	at 900° for 0.5 hr

* Thermally treated.

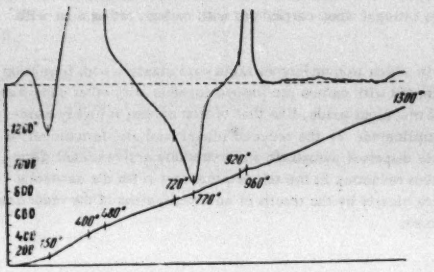


Fig. 8. Thermogram of Akkerman nickel cerolite.

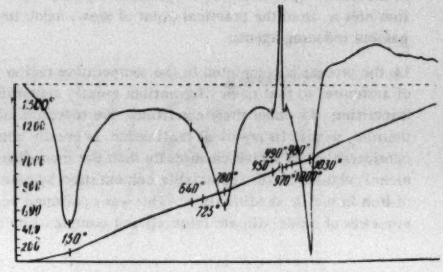


Fig. 9. Thermogram of Akkerman nickel dewylite.

All the investigated oxide-silicate minerals were reduced almost completely by hydrogen and by carbon monoxide in the temperature range 800-900°. Hence, in the process of direct gaseous reduction of complex iron ores, nickel can be almost completely reduced from all oxide and silicate minerals containing it at temperatures of about 900°, i.e., before sintering sets in the minerals that are to be reduced.

Investigation of the reduction of silicate minerals of nickel with carbon showed that this process becomes appreciable only at temperatures of about 770-800°, and becomes rapid only at temperatures at which crystallization effects occur in these minerals, so that the process tends to be inhibited. Under the conditions studied the maximum extents of reduction by carbon were as follows: a) for nepouite-garnierite – 83% at 1000° for 3 hours; b) for nickel dewylite – 69.0% at 1000° for 1 hour; c) for nickel cerolite – 47.8% at 1000° for 1 hour; and d) for nickel alumino-silicate – 73.7% at 1000° for 2 hours. Complete reduction of oxide-silicate minerals by carbon is not attained below the sintering temperature, and therefore the process of direct reduction with solid carbon is considerably inferior to the process of gaseous reduction in practicability and efficiency.

Investigation of the reduction process for eight different low-grade complex ores of iron-group metals from important worked deposits in the USSR showed that these ores can be reduced efficiently with gaseous reducers. At the beginning of the process of direct reduction, not only ferric oxide is reduced, but also non-siliceous oxide compounds of nickel, which are present in various amounts in these ores. The reduction of nickel from complex iron ores by means of hydrogen can therefore be detected to an appreciable extent already at 300°. Complete reduction of nickel from these oxide ores by means of hydrogen is attained at temperatures ranging from 400-500° to 800-900°, and the temperature for complete reduction bears an inverse relationship to the nickel content of the ore. Almost complete reduction of oxide-silicate ores with hydrogen is attained in the temperature range 900-1100°. Reduction of nickel from oxide complex ores with carbon monoxide becomes appreciable at 400°, and is almost complete at 600-700°, the temperature being dependent on the chemical and mineralogical compositions of the ore. Almost complete reduction of nickel from oxide-silicate ores by means of carbon monoxide is attained in the temperature range 900-1000°.

It was not found possible to reduce nickel with carbon from complex iron ores below the sintering temperature. The process of reducing complex iron ores with carbon before chemical-metallurgical treatment cannot therefore be recommended, for it is desirable to carry out this process without the sintering or melting of the ore to be reduced. Ferronickel reduced from complex iron ores with hydrogen has enhanced reactivity in various chemical-metallurgical processes, whereas ferronickel reduced from the ores with carbon monoxide or carbon is of low reactivity in such processes. Hence, when reduced ores are intended for subsequent chemical-metallurgical treatment with the object of the removal of gangue, it is undesirable to reduce them with carbon monoxide or carbon. The direct reduction of complex iron ores before chemical-metallurgical treatment should therefore be carried out with hydrogen, water gas enriched as much as possible in hydrogen, or natural and technical methane-containing gases after high-temperature conversion or cracking.

Apart from the proposed method of obtaining technical hydrogen from water gas, the following industrial methods of preparing hydrogen may be used: 1) conversion, i.e., reduction of steam with methane and other hydrocarbons (or carbon monoxide) at high temperatures; 2) cracking, i.e., thermal dissociation of methane at high temperatures; 3) the iron-steam method, i.e., thermal decomposition of steam under the action of iron at

high temperatures; 4) deep-freeze method; 5) electrolysis of water. Conversion and cracking are used for industrial and natural gases rich in methane and other hydrocarbons (and also carbon monoxide), but poor in nitrogen. The carbon dioxide obtained in the conversion process can be removed by washing with water at high pressure or by chemical absorption by ammonia and its compounds. The iron-steam method is associated with the necessity for periodic regeneration of the iron and is applicable to gases poor in methane, carbon monoxide, and hydrogen. The deep-freeze method is applicable to gases containing more than 50% of hydrogen (e.g., coke-oven gas). Electrolysis of water can be used in places where electrical energy is cheap.

Apart from purely gaseous reduction, combined processes may be of practical importance. Thus, according to the results of our investigations, the presence of steam and carbon dioxide in the reducing gas phase appreciably lowers the intensity of the reduction process, so that the introduction of some carbon (desirably peat coke) into the charge may be found to have a favorable effect. Such an addition will reduce the unfavorable effect of carbon dioxide and steam, which are always present in the sphere of reaction; these will react with carbon at high temperature with formation of carbon monoxide and hydrogen. This appears to be desirable also as a means for the removal of the deleterious effect of the air that is always present in the ore, and it is also desirable from the point of view of reducing any possible tendency for the ore to sinter at the temperatures required for the completion of the reduction of ores difficult to reduce. The drawing of air into the sphere of the reduction reaction, as may occur in practice, is by no means so harmful. Ground peat coke, and also reduced ferronickel, introduced into the ore to be reduced, has a catalytic accelerating effect at the appropriate high temperature on the conversion of methane and other hydrocarbons of industrial reducing gases, which are of low activity under the usual conditions. The hydrogen and carbon monoxide obtained in this way have an intensifying effect on the reduction processes.

Satisfactory plans for the complex direct reductions of iron ores may consist of specially designed multihearth roasters or rotary furnaces that ensure the attainment of the optimum conditions that we have established for the carrying out of this process on the large scale. A mechanical multihearth furnace has some advantages over a rotary furnace owing to the principle by which it operates; a more precise control can be kept over its functioning and it therefore gives more satisfactory trouble-free running under works conditions.

SUMMARY

1. Experimental and theoretical investigations were carried out on various processes for the complex direct reduction of multimetal iron and nickel ores, these processes being examined as a technological basis for the chemical treatment of the ores by methods that we have proposed.

2. This work established the theoretical and technological principles underlying the process of reducing these ores in such a way that the metals to be extracted show high reactivity in the subsequent chemical treatment.

3. The optimum conditions were found for carrying out the process efficiently under industrial conditions, and suggestions are made with regard to the plant required for the process.

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ELECTRON-MICROSCOPE INVESTIGATION OF POLISH SANDOMIR SILICAS

E. A. Leontyev, V. M. Lukyanovich, and Z. Ya. Sokalsky

The extensive literature on problems relating to carriers bears witness to the great importance of this question for heterogenous catalysis. There are some catalytic processes in which carriers are of special importance, in particular the Fischer-Tropsch process for the synthesis of hydrocarbons. There is an extensive patent literature on the preparation of carriers from silicas [1]. Teichner [2] showed that treatment of a filtration silica with acid resulted in a 50% increase in specific surface.

The results of Teichner's investigations have been confirmed by work at the Institute of Chemical Synthesis in Oswencim. In the work of Sokalsky, Szota [3], and others on silicas, acid treatments were used, and the effect of the method of treatment on the catalytic properties of the catalyst was confirmed.

It follows from Teichner's work that increase in specific surface occurs on account of the formation of small amounts of gel by the action of acid on silica. Confirmation of Teichner's views can be found in the electron-microscope results of Perroux [4]. Catalyst activity has been ascribed also to the formation of small amounts of hydroxyl compounds of cobalt, and increase in specific surface has been ascribed to the separation of chemically bound water in the process of reducing the catalyst.

Apart from the problem of the action of acids on silica, the effect of alkaline treatment on the carrier during the wet formation of the catalyst is also a very important problem for the elucidation of the catalytic process. No electron-microscope studies have yet appeared in the literature which could give information on the changes undergone by the carrier in alkaline media. It was this circumstance that prompted the present work.

EXPERIMENTAL

Polish silica of the following average composition was used for the investigations:

SiO_2	90.10 wt.%
Al_2O_3	4.02 wt.%
Fe_2O_3	2.31 wt.%
CaO	0.94 wt.%
MgO	0.24 wt.%
Ignition loss	2.07 wt.%
	99.68 wt.%

A more complete characterization of the silica is to be found in the literature cited [5].

Two methods of investigation were used in the study of silica under the electron microscope: the direct transmission method, and the indirect, replica method. In the first case, the pieces of silica were shaken in distilled water giving a partially colloidal suspension, and this was allowed to settle for about 20 minutes. Several drops were then taken by pipet from the upper layer of the suspension and transferred to a supporting film fixed to the grid of the object carrier. After being dried, the objects were examined in a UEM-100 electron microscope.

We used also the replica method, which has the advantage that information can be obtained about the surface relief of undamaged particles of the preparation. The preparation of replicas from a silica surface is associated with considerable difficulties owing to the low mechanical strength of the silica and its high porosity. We therefore rejected the usual method of two-stage replicas and developed a method of one-stage carbon replicas that is applicable to samples of this sort [6].

Plates (~ 5 × 10 × 10 mm) were split from a piece of silica and placed under a bell jar, which was evacuated. The fresh surface formed by splitting was sputtered with carbon. The distance from the sample to the carbons was

10 cm, the current was 30-50 amp, and the duration of sputtering was 1.5-2 minutes. The film so formed on the silica surface was cut into 3 x 3 mm squares by means of a lancet, and the plate was placed in hydrofluoric acid. After dissolution of the silica, a carbon film remained on the surface of the acid, and this was transferred, for washing, to another vessel of pure hydrofluoric acid with the aid of a loop of gold wire. The replica was then washed in hydrochloric acid and in water, removed on a copper grid, and shadowed with chromium.

Alkaline tratment was carried out by attaching a piece of the silica to a nylon thread and immersing it in 1% aqueous potassium hydroxide solution. After one minute, the sample was removed from the alkaline solution, carefully washed in distilled water, and dried at 105°. A carbon replica was then prepared from it by the method described above.

Let us consider the results obtained. As will be seen from Fig. 1, transmission photographs show the silica particles in the form of thin plates that are semitransparent to the electron rays. The edges of the plates are not sharp, and the plates themselves show in the photographs in varying contrast. It is probable that these plates have a layered structure and consist of still thinner leaves, so that the silica particles under examination are reminiscent of a pack of playing cards displaced with respect to the vertical axis. The preparation has a hydrophilic character and is fairly readily peptized by the simple action of water.

A different picture is observed in the case of the replicas (Fig. 2). Stereoscopic examination is very useful here, for flat representations cannot give an adequate idea of the character of the surface. An examination of stereoscopic photographs (Fig. 2a) shows that the cleavage surface of the silica has a very rough relief. Many protruberances of the order of one micron in size can be seen, and these are broken up by crevices varying in width and depth. In some cases the surface of these protruberances appears to be smooth; it is probable that the protruberances are formed of layers of the fine plates shown in Fig. 1, into which the preparation is broken down when dispersed in an aqueous medium. The highly developed crevice formation that can be readily seen in the photographs may explain the high porosity of the silica and its low mechanical strength.

After alkaline treatment, a sharp change occurs in the structure of the silica surface (Fig. 3). The characteristic protruberances and crevices disappear, the surface becomes much smoother, and many fine, almost spherical particles appear on the surface (in Fig. 3 they can be seen in the form of bright spots). The particles are fairly constant in size, the linear dimensions lying in the range 200-300 A for the great majority of them.

The sharp change that is observed to occur in the surface relief of the silica can be explained as follows. As a result of the alkaline treatment, a layer of alkali silicate is formed on the silica surface, and simultaneous smoothing of the surface occurs as a result of the dissolution of protruberances. During subsequent washing in water, potassium silicate is hydrolyzed with separation of silicic acid:

$$K_2SiO_3 + 2H_2O \rightleftharpoons H_2SiO_3 + 2KOH$$

The free silicic acid forms a colloidal solution, the particles of which cover the pieces of silica, filling the crevices and still further increasing the smoothness of the surface. In the drying of the preparation we obtain a surface layer formed from silicic acid gel, i.e., we are concerned essentially with the same process of hydrolysis of alkali silicate as is used for the preparation of silica gel. It may therefore be expected that the particles observed on the replicas taken from alkali-treated silica will be similar to the particles that form the usual silica gels. This supposition was confirmed by recently published work by two authors of the present paper, in which it was shown that silica gel has a corpuscular structure [7]. By way of example we show a photograph of a replica taken from coarsely porous silica gel, on which the particles forming the silica gel are visible in the form of bright spots (Fig. 4). The undoubted resemblance between Figures 3 and 4 is evidence in favor of the concepts we have described.

It may therefore be considered that alkaline treatment of silica results in covering of its surface with round particles of silicic acid gel and conversion of the surface silica layers into silica gel. This phenomenon may have a considerable effect on the characteristics of the catalysts obtained, which will be dependent on the degree of hydrolysis of the silicate and the structural peculiarities of the silica gel formed. The described method of investigation opens up new possibilities for the study of carriers and the appraisal of their suitability for the preparation of catalysts.

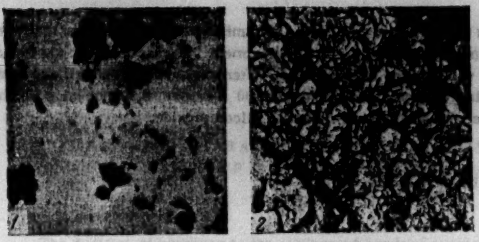

Fig. 1. Electron micrograph of particles of silica suspension (× 8200).

Fig. 2. Electron micrograph of silica surface (× 11,400).

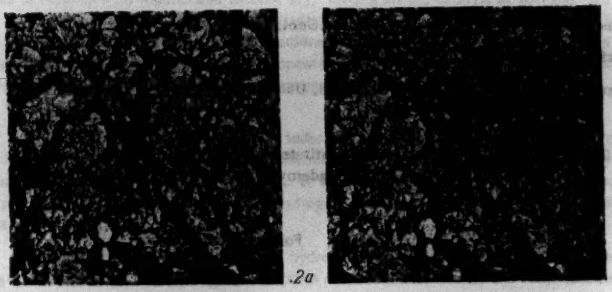

Fig. 2a. Stereoscopic electron micrograph of silica surface (× 11,400).

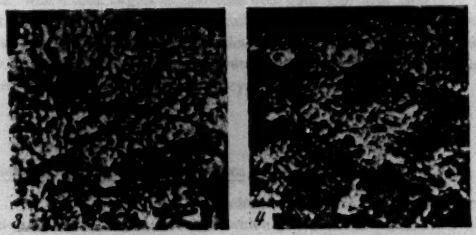

Fig. 3. Electron micrograph of silica surface after alkali treatment (× 60,000).

Fig. 4. Electron micrograph of the surface of coarsely porous silica gel (× 68,000).

SUMMARY

Silica was examined under the electron microscope – directly by transmission and indirectly in the form of carbon replicas – and the change in structure resulting from alkaline treatment was examined. It was found that the original silica has a lamellar structure with marked surface relief. After treatment with alkali and washing with water, its surface becomes covered with round particles about 100-200 A in size, a phenomenon which results from the hydrolysis of alkali silicate and separation of colloidal silicon dioxide.

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STAGEWISE CHARACTER OF THE HYDROGENATION OF THE DOUBLE BONDS OF CYCLOPENTADIENE OVER RANEY NICKEL

L. Kh. Freidlin and B. D. Polkovnikov

The addition of hydrogen to the conjugated bonds of cyclopentadiene has been studied by various investigators. When cyclopentadiene is hydrogenated in alcoholic solution with "hydrogen at the moment of its separation" obtained by the action of hydrochloric acid on zinc, a mixture containing small amounts of cyclopentene and cyclopentane is formed [1]. When reduced with active hydrogen formed by the action of calcium hexamoniate, cyclopentadiene is hydrogenated only as far as cyclopentene. However, the yield of cyclopentene is low: most of the cyclopentadiene is polymerized [2]. Considerable dimerization occurs also when cyclopentadiene is reduced with sodium and alcohol [3]. Over a nickel catalyst at 180-200° [4] and over platinized charcoal at 100° and higher [5,6], cyclopentadiene is hydrogenated to cyclopentane. Over Raney nickel [7] at a hydrogen pressure of 60-70 atm, cyclopentadiene is hydrogenated to cyclopentane even at room temperature. Hence, under these various conditions cyclopentadiene has been hydrogenated to a mixture of cyclopentene and cyclopentane and also exhaustively to cyclopentane.

In a short communication [3] it is indicated that with a deficiency of hydrogen, cyclopentadiene in absolute ethanol at room temperature in presence of Raney nickel is hydrogenated to cyclopentene, which was determined by the Raman spectrum method. It was noted also that the reaction rate changed sharply after the absorption of one molecular proportion of hydrogen. However, the experimental procedure and conditions are not described in detail.

In preliminary experiments on the hydrogenation of cyclopentadiene under similar conditions, no sharp change in the course of the hydrogen-absorption curve was observed by us. The addition of the second molecular proportion of hydrogen also proceeded at a high rate. In the present investigation we have studied the stagewise character of the hydrogenation of the conjugated double bonds of cyclopentadiene and the effect of the solvent on the reaction kinetics. Alcohols and hydrocarbons were used as solvents. Our kinetic investigation and our analytical results show that, in presence of Raney nickel at room temperature, the hydrogenation of cyclopentadiene does indeed proceed in two stages. At first the whole of the cyclopentadiene is hydrogenated to cyclopentene, which then begins to combine with hydrogen with formation of cyclopentane. In an alcoholic medium both stages are very rapid. In hydrocarbon solvents the second stage is slow and the kinetic curve for the overall process has a marked point of inflection corresponding to addition of 50% of the hydrogen. The steeply falling branch of the curve corresponds to hydrogenation of cyclopentadiene to cyclopentene, and the horizontal branch to hydrogenation of cyclopentene to cyclopentane.

EXPERIMENTAL

Procedure and Experimental Conditions

The cyclopentadiene was hydrogenated at 25° in a glass hydrogenation flask fitted with a water jacket and inlet and outlet tubes, in one of which a No.3 filter was sealed. The flask was 180 mm in length and 30 mm in diameter. Hydrogenation was considered to begin from the time when the shaker motor was switched on. When the reaction was very slow, it was not always carried to completion. Agitation was at 900 shakes per minute with a shaker amplitude of 12.7 cm. It was established by special experiments on the hydrogenation of cyclopentadiene in cyclohexane that such agitation is quite sufficient to ensure that reaction proceeds in the kinetic region.

The cyclopentadiene used (b.p. 41-42°; n_D^{20} 1.442—1.4446), was prepared by the depolymerization of the dimer. The catalyst was Raney nickel prepared by leaching a nickel-aluminum alloy (50%) with 20% sodium

hydroxide solution for two hours at 100°. A new 0.42 g portion of catalyst was used in each experiment. The hydrogen used was electrolytic and was freed from traces of oxygen. Before the reaction the catalyst was saturated with hydrogen under the conditions (same temperature, solvent, and rate of agitation) used for the hydrogenation. In the experiments carried out in hydrocarbon solvents the catalyst was washed from the spoon into the flask with the aid of 10 ml of alcohol, alcohol was poured off, the catalyst was washed twice with 10 ml portions of the relevant hydrocarbon, and a weighted amount of the substance to be hydrogenated in 10 ml of hydrocarbon solvent was introduced. All such operations (introduction and washing of catalyst, decanting and filtering, introduction of the substance to be hydrogenated, etc.) were carried out in a current of hydrogen. Reaction rate and catalyst activity were estimated from the rate of absorption of hydrogen.

Hydrogenation of Cyclopentadiene in Methanol

The alcohol used had b.p. 64.5° and n_D^{20} 1.3290. The results show that hydrogenation of cyclopentadiene in methanol at 25° proceeds rapidly and is complete in 8-9 minutes (Table 1, Experiments 1 and 2). The amount of hydrogen used corresponds to complete hydrogenation of both double bonds with formation of cyclopentane. The half-period of hydrogenation of cyclopentadiene sample (0.0019 mole) was 1.2-1.3 minutes, and 43 ml of hydrogen was absorbed in the first minute. About 6-8 minutes was required for the absorption of the second molecular proportion of hydrogen (47-49 ml). In methanol, therefore, both double bonds of cyclopentadiene are comparatively rapidly hydrogenated.

Figures 1-5 give the kinetic curves for the hydrogenation of cyclopentadiene. As will be seen from Fig. 1a, from the kinetic curve for the hydrogenation of cyclopentadiene in an alcoholic medium it is impossible to form an opinion about stagewise addition of hydrogen to the conjugated double bonds of cyclopentadiene. Hence, in order to establish the stagewise character of the hydrogenation of cyclopentadiene, experiments were carried out in which reaction was arrested after the addition of about 50% of the hydrogen; solution was separated from catalyst and was tested for the presence of cyclopentadiene by the hydroquinone reaction [8]. The reagent was prepared by dissolving 0.3 g of hydroquinone in 50 ml of methanol. In the test for cyclopentadiene 1-4 ml of reagent was generally taken, and 1-2 drops of 10% NaOH was added; in presence of cyclopentadiene the solution acquired an intense green color, and in its absence the methanolic hydroquinone gave an orange coloration.

Special experiments showed that the hydroquinone reaction is very sensitive and permits the detection of cyclopentadiene in mixtures containing less than 1%. One drop of a cyclopentadiene solution (0.12 g in 10 ml of methanol) gives a dark-green, almost black coloration. Even at a concentration of 0.6 mg in 10 ml of cyclohexane (i.e., 0.5%), the result is an orange solution that rapidly becomes brownish green. The color of the solution gradually changes into brown with formation of flocs. Cyclopentene and other olefins do not affect the color of hydroquinone in presence of alkali and do not interfere in the test for cyclopentadiene.

It was shown by the hydroquinone test that cyclopentadiene was absent form the solution after the consumption of about 50% of the amount of hydrogen required for the conversion of cyclopentadiene into cyclopentane (45-47 ml instead of 94-95 ml) (Table 1, Experiments 3 and 4). Hence, in methanol at 25° in presence of Raney nickel, the hydrogenation of cyclopentadiene proceeds in two stages. All the cyclopentadiene is first hydrogenated to cyclopentene, which then begins to combine with hydrogen with formation of cyclopentane.

In order to confirm that in alcoholic solution the second stage also proceeds rapidly, special experiments were carried out. The results showed that in methanolic and ethanolic media cyclopentene is indeed hydrogenated at a high rate (Experiments 15-18).

Hydrogenation of Cyclopentadiene in Ethanol

The kinetic curve for the hydrogenation of cyclopentadiene in 96% ethanol is given in Fig. 1c. Comparison with the kinetic curves for Experiment 1 (Fig. 1a) and Experiment 5 (Fig. 1b) shows that in absolute ethanol the hydrogenation of cyclopentadiene proceeds at about the same rate as in methanol. The consumption of hydrogen corresponds to complete hydrogenation of cyclopentadiene to cyclopentane. The half-period of reaction (hydrogenation to cyclopentene) is 1.5 minutes with an initial rate of hydrogen absorption of 35.2 ml/minute. In character the kinetic curve for the hydrogenation of cyclopentadiene in absolute ethanol is similar to the curve for hydrogenation in methanol; there is no point of inflection.

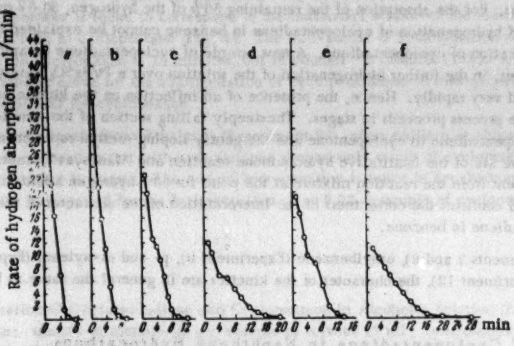

Fig. 1. Hydrogenation of cyclopentadiene: a) in methanol; b) in absolute ethanol; c) in 96% ethanol; d) in 75% ethanol; e) in isobutyl alcohol; f) in hexyl alcohol

In an aqueous-alcoholic medium the reaction rate is greatly reduced. Thus, comparison of the kinetic curve for Experiment 5 in absolute ethanol (Fig. 1b) with the curves obtained in Experiments 7 and 8 (Figures 1c and 1d) in an aqueous-alcoholic medium shows that in 96% alcohol the rate of reaction is about 35% lower, and in 75% alcohol it is about 65% lower, than in absolute alcohol. In the case of 75% alcohol, the kinetic curve (Fig. 1d) shows a distinct inflection at the point corresponding to the absorption of 38.4 ml of hydrogen – which corresponds to about 50% of the hydrogen necessary to saturate the given sample of cyclopentadiene. The half-period of hydrogenation is 5 minutes. From this point the rate of hydrogen absorption falls: the second section of the curve is less steep than in the case of 96% ethanol. It may be supposed that the steeply falling part of the kinetic curve corresponds to hydrogenation of cyclopentadiene to cyclopentene, whereas the gently falling part represents the slower hydrogenation of the cyclopentene formed into cyclopentane. It was confirmed by the qualitative test that at the moment corresponding to the point of inflection on the kinetic curve cyclopentadiene was absent from the solution (Experiment 9).

Hydrogenation of Cyclopentadiene in Isobutyl, tert-Butyl, and Hexyl Alcohols.

The alcohols used had the following constants: isobutyl alcohol, b.p. 108°, n_D^{20} 1.3952; tert-butyl alcohol, b.p. 83°, n_D^{20} 1.3880; hexyl alcohol (fraction of b.p. 152-155° (743 mm) and n_D^{20} 1.4188).

In isobutyl alcohol (Table 1, Experiment 14) reaction proceeds at almost the same rate as in 96% ethanol (Fig. 1e). In tert-butyl and hexyl alcohols (Experiments 10 and 12) the rates of hydrogenation of cyclopentadiene are identical and are appreciably lower than in ethyl and isobutyl alcohols. The theoretically necessary amount of hydrogen adds in 30 minutes. The half-period of hydrogenation is 5 minutes. There is no inflection on the curve at the point for 50% addition of hydrogen (Fig. 1f). The qualitative reaction with hydroquinone showed that, in these solvents also, hydrogenation of cyclopentadiene proceeds in stages (Experiments 11-13).

Hydrogenation of Cyclopentadiene in Aromatic Hydrocarbons

The solvents used had the constants: benzene (thiophene-free), b. p. 79.6-80.6°, n_D^{20} 1.5008; toluene, b. p. 110.5°, n_D^{20} 1.4954; ethylbenzene, b. p. 136°, n_D^{20} 1.4960; isopropylbenzene (fraction of b. p. 150-151° treated with sulfuric acid; n_D^{20} 1.4910); m-xylene, b. p. 139°, n_D^{20} 1.4974; p-xylene, b. p. 138°, n_D^{20} 1.4960.

The kinetic curve for the hydrogenation of cyclopentadiene in benzene is given in Fig. 2a. The character of the kinetic curve for the hydrogenation of cyclopentadiene is benzene differs greatly from that for reaction in methyl and ethyl alcohols. The curve has a marked inflection at the point for the absorption of 47-50 ml of hydrogen, which is about 50% of the amount required to saturate the cyclopentadiene taken. After the point of inflection the rate of hydrogenation falls sharply.

As shown by the data in Table 2 (Experiments 4, 5, and 6), the half-period for hydrogenation of cyclopentadiene in benzene is 4 minutes. For the absorption of the remaining 50% of the hydrogen, 30-32 minutes is required. Such a reduction of the rate of hydrogenation of cyclopentadiene in benzene cannot be explained by poisoning of the catalyst owing to the polymerization of cyclopentadiene. A new sample of cyclopentadiene is rapidly hydrogenated on the used catalyst. Moreover, in the further hydrogenation of the solution over a $Pt/BaSO_4$ catalyst, the remaining 47-50 ml of hydrogen is absorbed very rapidly. Hence, the presence of an inflection on the kinetic curve and its position are due to the fact that the process proceeds in stages. The steeply falling section of the kinetic curve represents the hydrogenation of cyclopentadiene to cyclopentene and the gently sloping section represents addition of hydrogen to cyclopentene. With the aid of the qualitative hydroquinone reaction and Afanasyev's reaction [10] it was shown that cyclopentadiene is absent from the reaction mixture at the point for 50% hydrogen addition. This indicates the selectivity of the process and confirms the correctness of our interpretation of the character of the kinetic curve for the hydrogenation of cyclopentadiene in benzene.

In toluene (Experiments 7 and 8), ethylbenzene (Experiment 9), p- and m-xylenes (Experiments 10 and 11), and isopropylbenzene (Experiment 12), the character of the kinetics are in general the same as in benzene (Figures 2b, 2c, 2d, 2e, and 2f).

Hydrogenation of Cyclopentadiene in Naphthene Hydrocarbons

The cyclohexane used as solvent had b.p. 81° and n_D^{20} 1.4266. In cyclohexane, as also in benzene, hydrogenation of cyclopentadiene is considerably slower than in methanol. The kinetic curve for the hydrogenation of cyclopentadiene in cyclohexane is similar to the curve for its hydrogenation in benzene, but in the first case the inflection corresponding to addition of one molecular proportion of hydrogen is more sharply marked.

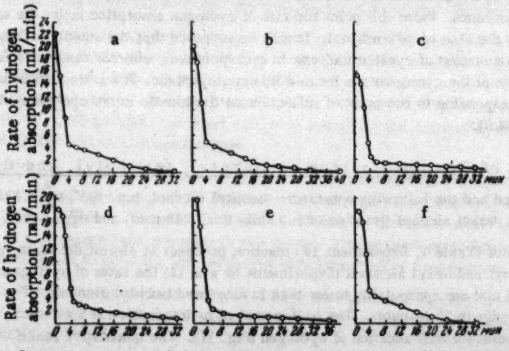

Fig. 2. Hydrogenation of cyclopentadiene: a) in benzene; b) in toluene; c) in ethylbenzene; d) in p-xylene; e) in m-xylene; f) in isopropylbenzene.

It was shown by Shuikin's [9] and Afanasyev's [10] qualitative reactions, and also by the hydroquinone method, that at the point at which about 50% hydrogen addition occurred in Experiments 18 and 19 (Table 2) cyclopentadiene was indeed absent from the solution. At 46-47% hydrogenation the reaction for cyclopentadiene was positive. Hence, again in cyclohexane stepwise saturation of the conjugated double bonds of cyclopentadiene occurs.

The sharp reduction in reaction rate after the absorption of 50% of the total amount of hydrogen required is due to the low rate at which cyclopentene is hydrogenated in cyclohexane. It was shown by special experiments

that, unlike the addition of hydrogen to cyclopentene in an alcoholic medium, addition of hydrogen in a cyclohexane medium is indeed very slow (Table 2, Experiment 24), and the character of the kinetic curve for the hydrogenation of cyclopentene is found to correspond to the horizontal section of the kinetic curve for the hydrogenation of cyclopentadiene to cyclopentane (Fig. 4). The half-period of hydrogenation of a sample of cyclopentene (0.0019 mole) in cyclohexane is 18 minutes, but in ethanol – 2 minutes (Table 2, Experiments 17 and 18). The character of the kinetic curve for the hydrogenation of cyclopentadiene in methylcyclohexane (Experiments 20 and 21) is the same as that for cyclohexane.

In an experiment with decahydronaphthalene (Experiment 22), after addition of about 50% of the total amount of hydrogen required, a qualitative test with hydroquinone showed only traces of cyclopentadiene in the solution, i.e., hydrogenation proceeded in stages. The rate of hydrogenation is lower in decahydronaphthalene than in cyclohexane. Thus, the half-period for the hydrogenation of an 0.08 g sample of cyclopentadiene was 11 minutes.

TABLE 1

Hydrogenation of Cyclopentadiene and Cyclopentene in Alcoholic Solution (Experimental conditions: sample of nickel 0.42 g; volume of solvent 10 ml; temperature 25°; rate of agitation 900 shakes per minute)

Experiment	Solvent	Weight of substance	Initial rate of hydrogen absorption (ml/min)	Total duration of reaction (minutes)	Half-period of reaction (minutes)	Degree of hydrogenation of cyclopentadiene (%)	Qualitative test for cyclopentadiene
			Cyclopentadiene				
1	Methanol	0.1288	42.8	9	1.2	—	—
2	"	0.1243	40.7	8	1.3	—	—
3	"	0.1224	46.1	—	—	50.6	Negative
4	"	0.1239	—	—	—	48.1	Negative
5	Ethanol (absolute)	0.1208	35.2	10	1.5	—	—
6	Ethanol (96%)	0.1286	22.4	14	2.4	—	—
7	"	0.1240	22.8	12	2.3	—	—
8	Ethanol (75%)	0.1176	11.5	—	5.0	—	—
9	Ethanol (96%)	0.1289	25.9	2.5	—	53.6	Negative
10	tert-Butyl alcohol	0.1231	11.0	30	5.0	—	—
11	" "	0.1261	9.9	7	—	59.3	Negative
12	Hexyl alcohol	0.1212	10.6	30	5.0	—	—
13	" "	0.1212	10.1	7	5.0	56.7	Negative
14	Isobutyl alcohol	0.1280	16.5	14	3.0	—	—
			Cyclopentene				
15	Methanol	0.1318	20.5	6	1.2	—	—
16	"	0.1240	21.5	6	1.1	—	—
17	Ethanol	0.1311	13.5	7	1.9	—	—
18	"	0.1311	13.6	8	1.9	—	—

Hydrogenation of Cyclopentadiene in Heptane

The heptane had b. p. 98.4° and n_D^{20} 1.3880. The kinetic curve for the hydrogenation of cyclopentadiene in heptane is given in Fig. 5. It will be seen from Fig. 5 that the kinetic curve is similar to that obtained for reaction in cyclohexane. The process proceeds in stages. The first stage – hydrogenation to cyclopentene – proceeds at about the same rate as in absolute ethanol. The second stage – the hydrogenation of the cyclopentene formed into cyclopentane – proceeds very slowly in heptane solution.

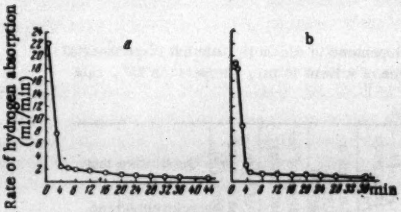

Fig. 3. Hydrogenation of cyclopentadiene: a) in cyclohexane; b) in methylcyclohexane.

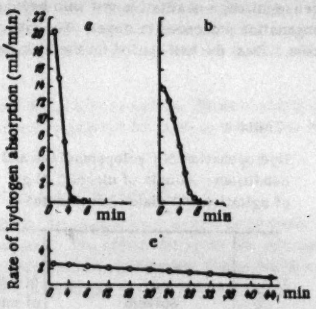

Fig. 4. Hydrogenation of cyclopentadiene: a) in methanol; b) in ethanol; c) in cyclohexane.

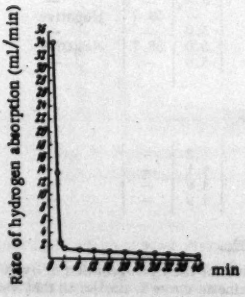

Fig. 5. Hydrogenation of cyclopentadiene in heptane.

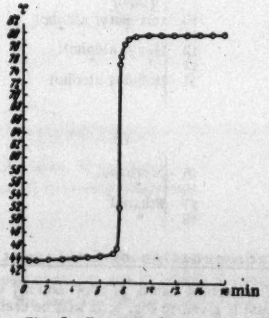

Fig. 6. Fractionation curve.

Possibility of the Practical Preparation of Cyclopentene by the Partial Hydrogenation of Cyclopentadiene

As shown above, with small samples of cyclopentadiene it is easy to bring about hydrogenation in stages. It was of interest to determine whether it is possible to apply this method to the preparation of cyclopentene, which is generally prepared by a multistage synthesis from adipic acid. With this object, cyclopentadiene was hydrogenated in several portions, and in all 7.6284 g was hydrogenated with agitation in presence of 1.7 g of catalyst. After 50% of the theoretically necessary hydrogen (3450 ml) had been consumed, reaction slowed down considerably, and the reaction was interrupted. A test for cyclopentadiene was negative. The hydrogenation product was fractionated through a 30-plate column. The fractionation curve is given in Fig. 6. A fraction (5.4718 g) of b.p. 43.4-44.9° and n_D^{20} 1.4202 was isolated. The content of unsaturated hydrocarbons was 94%, and in the hydrogenation of 0.2596 g in presence of Raney nickel and ethanol at 20°, 88.1 ml of hydrogen was consumed instead of the 96.4 ml theoretically required. These properties of the hydrogenation product are close to those of cyclopentene. In this exploratory experiment, therefore, stagewise hydrogenation of the bonds of cyclopentadiene is found to be preserved when a large sample of the diene is hydrogenated.

TABLE 2

Hydrogenation of Cyclopentadiene and Cyclopentene in Hydrocarbon Solvents (Experimental conditions: sample of nickel 0.42 g; volume of solvent 10 ml; temperature 25°; rate of agitation 900 shakes per minute)

Experiment	Solvent	Weight of substance	Initial rate of hydrogen absorption (ml/min)	Total duration of reaction (min.)	Half-period of reaction (min.)	Consumption of H before inflection pt. (ml)	Calculated H (ml)	Degree of hydrogenation of cyclo- (%)	Qualitative test for cyclopentadiene
			Cyclopentadiene						
1*	Cyclohexane	0.1192	10.2	—	6.0	47.2	92.1	—	—
2**	"	0.1192	16.5	—	3.5	48.4	92.1	—	—
3***	"	0.1270	16.6	—	5.0	50.9	98.3	—	—
4	Benzene	0.1283	17.7	35	4.0	50.7	99.1	—	—
5	"	0.1234	22.0	33	3.5	47.9	95.1	—	—
6	"	0.1244	16.3	36	4.0	49.5	97.0	—	—
7	Toluene	0.1235	—	35	3.5	49.0	99.8	—	—
8	"	0.1299	—	35	3.6	50.4	103.2	—	—
9	Ethylbenzene	0.1242	15.3	—	4.5	47.8	97.2	—	—
10	m-Xylene	0.1486	18.1	47	4.5	56.8	115.0	—	—
11	p-Xylene	0.1247	19.6	—	4.2	48.5	96.7	—	—
12	Isopropylbenzene	0.1254	—	36	3.5	47.7	98.5	—	—
13	Cyclohexane	0.1333	22.0	54	3.5	51.4	103.4	—	—
14	"	0.1183	20.6	—	4.0	46.4	91.4	—	—
15	"	0.1232	17.7	—	3.5	49.0	96.6	—	—
16	"	0.1271	15.5	—	5.0	49.0	98.2	—	—
17	"	0.1226	17.6	7	—	—	94.7	46.0	Positive
18	"	0.1400	—	8	—	—	107.7	50.7	Negative
19	"	0.1263	—	—	—	—	98.4	46.9	Positive
	"	0.1297	—	7	—	—	100.7	48.3	Negative
20	Methylcyclohexane	0.1266	22.2	—	4.0	50.0	100.2	—	
21	"	0.1266	18.6	—	4.0	48.2	100.2	—	
22	Decahydronaphthalene	0.0804	7.4	—	11.0	—	62.6	48.6	Traces
23	Heptane	0.1246	34.3	31	2.5	50.1	96.3	—	
			Cyclopentane						
24	Cyclohexane	0.1290	2.1	—	18.0	—	48.5	—	—

* At a rate of agitation of 480 shakes per minute.

** At a rate of agitation of 620 shakes per minute.

*** At a rate of agitation of 840 shakes per minute.

SUMMARY

1. An investigation was made into the kinetics of the hydrogenation of cyclopentadiene in presence of Raney nickel at 25° and normal pressure in alcoholic and hydrocarbon solutions.

2. It was shown that cyclopentadiene is rapidly hydrogenated to cyclopentane in methyl, ethyl, and isobutyl alcohols.

3. In aromatic, hydroaromatic, aliphatic hydrocarbon solutions, cyclopentadiene is rapidly hydrogenated only as far as cyclopentene, and the second molecular proportion of hydrogen adds very slowly.

4. In all solvents examined, the conjugated double bonds of cyclopentadiene are hydrogenated successively. In hydrocarbon solvents the two-stage character of the process can be demonstrated also by kinetic methods.

5. Both in alcohol and in hydrocarbon solvents cyclopentene can be obtained from cyclopentadiene if the hydrogenation is arrested after the addition of one molecular proportion of hydrogen.

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CATALYTIC ACTIVITY AND ACIDITY OF SILICA GEL TREATED WITH SOLUTIONS OF ALUMINUM SALTS

K. G. Miesserov

Acidic aluminosilicates are able to catalyze cracking reactions, polymerizations, redistribution of hydrogen, and various other reactions [1-5]. We have shown that the catalytic activity of aluminosilicates in the reaction of redistribution (disproportionation) of hydrogen is determined only by ions having exchange and hydrolytic acidity. It was established that a linear relationship exists between the amount of sodium ions absorbed from sodium chloride and sodium acetate solutions and the degree of conversion of cyclohexene (the extent of formation of saturated hydrocarbons), and this enabled us to determine, by extrapolation, the acidity characterizing the activity of the aluminosilicate catalyst [6].

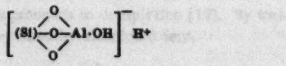
However, the catalytic effects of various samples of aluminosilicates may not be proportional to the acidity determined in this way inasmuch as the activity of an aluminosilicate is determined not only by the chemical properties of its surface, but also by other, purely physical factors, such as its surface area and the character of its porosity. Silica gel is not a catalyst for the reactions mentioned above, but it becomes catalytically active after activation with aluminum ions*.

Frost and coworkers [8] showed that, in the activation of silica gel with alumina, the surface area and porosity characteristics of the gel were not affected. Hence, the varying activities of samples having various aluminum contents must be due entirely to different degrees of acidity.

EXPERIMENTAL

Samples of silica gel containing various amounts of alumina were prepared by treating finely porous KSM silica gel, which had been roasted at 450° for three hours, with aluminum salts by the following methods: 1) treatment with aluminum nitrate solutions of various concentrations and subsequent washing with water until the washings ceased to give a reaction for nitrate; 2) impregnation with a definite amount of concentrated aluminum nitrate solution; 3) treatment with $NAlCl_3$ neutralized to the extent of 25% with N NaOH** and subsequent washing with water until the the washings ceased to give a reaction for chloride; 4) treatment with a suspension of barium carbonate in N NaCl with subsequent displacement of absorbed sodium ions by aluminum ions by treatment with aluminum nitrate solution and washing with water to remove excess of salt. The duration of treatment and the volumes of the solutions of aluminum salts were also varied. The samples were dried at 100° and roasted for three hours at 450°. Some samples were prepared by treating coarsely porous silica gel with aluminum salts.

* The active complex formed in the activation of silica gel with aluminum ions is of the following form [7]



** When the sodium hydroxide solution is added to the aluminum chloride solution, a precipitate of aluminum hydroxide is formed, but this ultimately vanishes owing to the conversion of aluminum hydroxide into soluble basic aluminum compounds.

The aluminum contents and the exchange and hydrolytic acidities of the samples were determined by the methods described in previous papers [9,10]. The degree of conversion of cyclohexene (amount of saturated hydrocarbons formed) was taken as a measure of catalytic activity. The experiments were carried out in the usual apparatus employed for the study of catalytic processes during continuous flow.

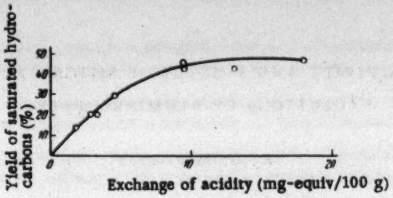


Figure. Relation between the degree of conversion of cyclohexene and the exchange acidity of the samples of aluminosilica gel.

Table 1 gives the values of the exchange and hydrolytic acidities of the aluminosilica gel samples and the degree of conversion of cyclohexene in their presence.

It will be seen from the results that the activities of the samples are not characterized by the values of their hydrolytic acidity: the hydrolytic activities of samples treated with aluminum nitrate solutions did not differ from the hydrolytic acidity of the original silica gel. We therefore attempted to establish the character of the relationship between activity and exchange acidity.

A graph was constructed from the data in Table 1, the abscissae representing exchange acidity and the ordinates percent of saturated hydrocarbons formed. We see that catalytic activity is at first approximately proportional to exchange activity, but the slope of the curve then diminishes and it becomes almost parallel to the axis of abscissae.

TABLE 1

Acidity and Activity of Silica Gel Treated with Aluminum Salts

(Hydrolytic activity of original silica gel 27.6 mg-equiv/100 g. Experimental conditions in catalytic conversion: temperature 316°; volume of catalyst 30 ml; space velocity 2 hour $^{-1}$)

Method of activation		Exchange acidity (mg-equiv/100 g	Hydrolytic acidity mg-equiv/100 g	Yield of saturated hydrocarbons (%)
Treated with $Al(NO_3)_3$ solution	0,1 *N*	1.8	27.6	13.8
	0,2 *N*	3.0	27.6	20.9
	1,0 *N*	3.5	27.6	21.2
Impregnated with $Al(NO_3)_3$, solution so as to apply	1%	4.6	29.4	29.9
	3%	9.6	33.6	44.4
Treated with N $AlCl_3$ 25% neutralized with N NaOh for	1	9.6	34.2	42.8
	3 "	13.0	35.9	42.5
	7 "	18.0	39.6	47.2

We have attempted to explain the results of our experiments as follows. We have previously suggested [11], that silica gel surfaces contain hydroxyls as isolated groups and as pairs*. The two hydroxyls of each pair are equivalent, but if the hydrogen of one of the hydroxyls is replaced by a metal ion, the activity of the second hydroxyl falls, for the part of the silica gel structure in which the two hydroxyls occur attached to a silicon atom may be regarded as a dibasic acid for which the constant of the first stage of dissociation is much greater than that of the second.

Hence, only one of the hydroxyls of a paired group is active, and the second hydroxyls and isolated hydroxyls are inactive. The number of active hydroxyls is taken into account in the value of the hydrolytic acidity. When silica gel is treated with aluminum nitrate solutions, only a part of the active (hydrolytic) hydroxyls reacts. The hydrolytic acidity does not change, for the number of active aluminum ions displaced into the sodium acetate solution is equal to the number of hydrogen ions replaced by them. In this case, the hydrolytic acidity is the sum of the displaced hydrogen and aluminum ions, and catalytic activity increases as the proportion of aluminum ions in this sum increases. Maximum activity should be found in the sample in which hydrogen ions are replaced by aluminum ions in all hydrolytic hydroxy groups. It will in fact be seen from Table 2 that the sample obtained by treating silica gel with a suspension of barium carbonate in N NaCl and then with aluminum nitrate solution** and containing only active aluminum ions in amount closely equivalent to the hydrolytic acidity of the original silica gel had an activity close to the maximum obtained.

TABLE 2

Degree of Conversion of Cyclohexene over Aluminosilica Gel Having Various Aluminum Contents (Experimental conditions: temperature 320°; volume of catalyst 20 ml; space velocity 2 hour^{-1})

Method of activation		Aluminum content mg-equiv/100 g	Yield of saturated hydrocarbons (%)
Treated with $Al(NO_3)_3$ solution	0.1 N	6.5	16.8
	0.1 N	8.9	20.8
	1.0 N	12.4	28.2
Treated with suspension of $BaCO_3$ in N NaCl and then with N $Al(NO_3)_3$ for	2 days	17.2	37.6
	5 "	27.2	48.3
Impregnated with $Al(NO_3)_3$, solution so as to apply	1%	58.8	39.1
	3%	176.4	47.9
Treated with N $AlCl_3$ 25% neutralized with N NaOh for	1 day	64.2	48.7
	7 "	84.5	55.7

* We consider paired and isolated hydroxyls to correspond to the structures $>Si\langle^{OH}_{OH}$ and $-\overset{|}{Si}-OH$ respectively.

** By treatment of silica gel with a suspension of barium carbonate in sodium chloride solution, complete replacement of the active hydrogen ions with sodium ions can be attained because the acid liberated is neutralized by barium carbonate and reaction proceeds to completion [12]. By treatment with aluminum nitrate solution, the absorbed sodium ions are then replaced by aluminum ions.

All the active aluminum ions in a given sample of catalyst are equivalent: this is proved by experiments on the poisoning of aluminosilicate catalysts with sodium ions and pyridine [6,13]. This equivalence shows itself only at high temperatures under catalysis conditions. In an aqueous medium the active aluminum ions show variation in mobility: for example, not all of them can be replaced by sodium ions of NaCl solutions.

Increase in the amount of aluminum absorbed by silica gel may result in increase in exchange acidity not only because of increase in the number of active aluminum ions, but also because of increase in the mobility* of the already existing active aluminum ions in an aqueous medium: an aluminum ion, in taking up its place in the vicinity of an active aluminum ion, increases the mobility of the latter [11]. Hence, increase in exchange acidity does not necessarily result in a proportionate increase in catalytic activity.

The absorption of aluminum by silica gel during treatment with a solution of an aluminum salt proceeds as a result of interaction between hydroxyls of the silica gel and basic aluminum compounds [11,14]. In the sample prepared by impregnation with aluminum nitrate solution, not all of the aluminum is chemically bound to the silica gel: part of it is in the form of alumina and does not contribute to an increase in catalytic activity. Treatment with aluminum chloride solution that is partially neutralized with sodium hydroxide ensures that the whole of the aluminum absorbed becomes chemically bound to the silica gel. This is found to be the most efficient treatment. For example, a sample of coarsely porous silica gel (Table 3) obtained by impregnation with aluminum nitrate solution was almost inactive,, but the activity, calculated per unit weight, of a sample prepared by treatment of coarsely porous silica gel with aluminum chloride solution partially neutralized with sodium hydroxide was found to be even more active than finely porous silica gel activated by the same method. A sample treated in this solution should have maximum activity because all hydrogen ions in its active hydroxy groups are replaced by aluminum ions in such a treatment, i.e., the sample contains the maximum possible number of active aluminum ions. However, the data in Tables 1 and 2 show that with increase of the duration of treatment with fresh portions of the solution, the activity continues to increase somewhat. This is probably due to the fact that increase in the ability of active aluminum ions to undergo exchange partially affects catalytic activity, this being determined not only by the value of the acidity, but also by the dissociation constant of the acid.

TABLE 3

Degree of Conversion of Cyclohexene over Coarsely Porous and Finely Porous Aluminosilica Gels (Experimental conditions: temperature 316°; volume of catalyst 30 ml; space velocity 2 hour^{-1})

Method of activation	Silica gel sample	Weight of sample taken for experiment	Exchange acidity (mg-equiv/100 g	Yield of saturated hydrocarbons (%)	Yield of saturated hydrocarbons per 100 g of sample (%)
Impregnated with $Al(NO_3)_3$ solution so as to apply 3% Al_2O_3	Finely porous	25.0	9.6	44.4	17.7
	Coarsely porous	13.3	9.6	2.4	1.8
Treated with N $AlCl_3$ 25% neutralized with N NaOH for 3 days	Finely porous	24.2	9.6	42.8	17.7
	Coarsely porous	14.2	12.7	20.7	14.6
		23.8			
Treated with N $AlCl_3$ 25% neutralized with N NaOH for 7 days	Finely porous	14.8	18.0	47.2	19.8
	Coarsely porous		18.0	31.9	21.5

* Mobility is here understood to mean the ability of cations attached to a silica gel surface to undergo exchange with cations of a neutral salt.

SUMMARY

1. Increase in the catalytic activity of preparations obtained by treatment of silica gel with solutions of aluminum salts is not proportional to the increase in their exchange acidity, for the ability of active aluminum ions to undergo exchange increases more rapidly than the number of these ions.

2. Silica gel acquires catalytic activity as a result of replacement of hydrogen ions by aluminum ions in hydrolytic hydroxy groups only.

3. Activation of silica gel by treatment with solutions containing basic aluminum salts is considerably more effective than activation by application of alumina.

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INVESTIGATION WITH THE AID OF LABELED ATOMS OF THE CONDITIONS REQUIRED FOR THE SEPARATION OF ZINC AND COBALT FROM ALUMINUM AND IRON

Yu. V. Morachevsky and Z. S. Bashun

The separation of tervalent ions from bivalent ions is frequently carried out in the complete analysis of minerals, rocks, and many industrial products. Many of the methods of separation are based on the precipitation under various pH conditions, of hydroxides and basic salts of the elements to be separated. This principle lies at the basis of the precipitation of hydroxides and basic salts of ter-and quadri-valent ions from the buffer solutions ammonia + ammonium salt (the widely practiced precipitation with ammonia) and ammonium acetate + acetic acid (the so-called "acetate hydrolysis" method), and it lies also at the basis of precipitation with weak organic bases, etc.

The conditions required for maximum completeness of separation have frequently attracted the attention of investigators. However, the detailed elucidation of the effect of individual factors on completeness of separation and the complicating phenomenon of coprecipitation was rendered difficult by the complexity and insufficient sensitivity of methods of determining the distribution of the particular ion between precipitate and solution.

There are wide possibilities for the application of radioactive isotopes to the accurate determination of the behavior of an ion in various analytical separations. In our opinion, one of the urgent tasks of modern analytical chemistry is the detailed study, with the aid of labeled atoms, of the methods of ion separation used in analytical practice with the object of revealing sources of error and methods of avoiding error. Work in this direction has already begun [1,2].

In the present paper we give the results of an investigation of three methods of separating aluminum and iron from zinc and cobalt: 1) precipitation of hydroxides of tervalent metals with ammonia; 2) so-called "acetate hydrolysis"; and 3) precipitation of aluminum and iron with pyridine. These particular bivalent ions were selected because conditions for their separation have received very little investigation.

The precipitation of the hydroxides of aluminum, iron, and titanium with ammonia in order to separate these elements from manganese, calcium, and magnesium is extensively used in the analysis of silicates. The conditions for separation were studied very fully by Blum [3], who recommended precipitation from hot solutions containing a sufficient amount of ammonium salts, the pH of the solution being maintained at 6-6.5 with the aid of Methyl red. The conditions recommended by Blum for the precipitation of aluminum and iron hydroxides have been accepted by most authors of later publications. Hillebrand and Lundell [4] also recommend the precipitation conditions proposed by Blum, though they point out that complete separation of aluminum and iron from zinc, cobalt, and copper is not attained even when the precipitate of hydroxides is reprecipitated; they cite the results of Lundell and Knowles [5], which characterize the degree of entrainment of various bivalent ions by precipitates of aluminum hydroxide formed under Blum's conditions.

The method of so-called "acetate hydrolysis" consists in boiling a very dilute ammonium acetate + acetic acid buffer solution containing tervalent iron, aluminum, and titanium, which are precipitated as sparingly soluble basic acetates. As precipitation occurs at relatively low pH (5.2-5.6) [6], it may be expected that, after reprecipitation, the precipitate will not contain bivalent ions, including those in which we are interested,

zinc and cobalt. This method is often recommended for the separation of iron and aluminum from bivalent ions; its main defect is incomplete precipitation of aluminum, it being generally recommended that its precipitation be completed in the filtrates after the separation of the main precipitate, for which purpose the filtrates are evaporated down to small bulk and their pH is increased somewhat by addition of ammonia [7]. Lassieur [8] considers that complete precipitation of aluminum as basic acetate is attained at pH not less than 5.3.

The use of pyridine for the separation of tervalent ions from bivalent is considered in a series of papers by Ostroumov and coworkers [9-12]. Being a weak base, pyridine precipitates aluminum and ferric hydroxides, whereas it forms soluble complex compounds with several bivalent ions. In order to maintain zinc in solution it has been proposed that a large amount of ammonium chloride be added.

EXPERIMENTAL

1. Behavior of Zinc and Cobalt in the Precipitation of Aluminum and Ferric Hydroxides with Ammonia

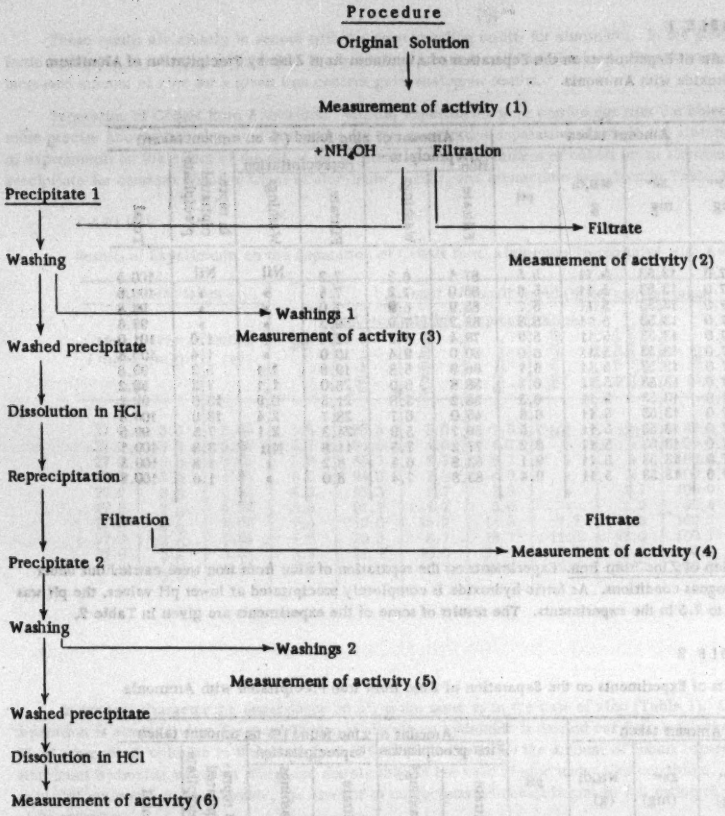
A definite amount of the radioactive isotope of zinc or cobalt (Zn^{65} or Co^{60}) was introduced into a solution containing known amounts of aluminum or iron and zinc or cobalt in the form of chlorides. The original solution, prepared in this way, was always 100 ml in volume. The solution was heated to the boil, and aluminum or ferric hydroxide was precipitated with ammonia. After ten minutes the hot solution was filtered and the residue was washed with 2% ammonium nitrate solution; the main filtrate and washings were collected separately. The volume of the washings, like that of the original solution, was 100 ml. Activity measurements were made on the filtrate and washings, and the pH of the main filtrate was determined - generally with a quinhydrone electrode, and in control experiments with a hydrogen electrode. The precipitate of hydroxide was dissolved in dilute hydrochloric acid, and aluminum (or ferric) hydroxide was reprecipitated under the same conditions as in the first precipitation. The filtrate and washings were collected separately, each was made up to 100 ml, and their activities were measured. The reprecipitated material was redissolved and its activity was measured.

Thus, activity measurements were taken only on solutions. For this purpose the solutions were placed in glass vessels having two walls of thin glass; 20 ml of solution was always taken. The counter tube was fixed vertically, and the vessel was placed on it. Before each measurement the background of the apparatus and vessel (filled with water) was checked: it was fairly great, but stable, varying between 38 and 41 impulses per minute. In the measurement of the activity of the solutions under investigation, counts were taken over 5-15 minutes, depending on the activity; in the case of very low activity, the count was continued until the total number of impulses registered reached 500. A correction for background was always made to the results of the count. The procedure is outlined schematically on the following page.

Separation of Zinc from Aluminum. The first series of experiments had the object of determining the effect of the pH of the solution on the coprecipitation of zinc with aluminum hydroxide. The contents of aluminum and zinc were not varied. The results are given in Table 1.

It will be seen from Table 1 that complete separation of aluminum and zinc under the selected conditions (identical with those recommended by Blum) is attained only at pH values lying within very narrow limits, 5.5-5.8. With rise in pH to about 7, the zinc content of the reprecipitated precipitate increases; with further rise in pH the amount of zinc carried down with the precipitate begins to diminish owing to partial formation of a zinc ammine; at pH 9.4 (considerable excess of ammonia) the precipitate contains only 1.6% of the whole of the zinc. Further rise in pH is made difficult by the buffering action of the ammonium salt, but it is of no practical interest since the precipitation of aluminum was found to be incomplete under these conditions.

Ammonium chloride, apart from having a buffer action and improving conditions for coagulation of the hydroxide, reduces coprecipitation of zinc due to exchange adsorption. Special experiments showed that reduction of the concentration of ammonium salt without change in other conditions results in increase in the entrainment of zinc by the precipitate; on the other hand, increase in the concentration of ammonium chloride beyond 5% had no effect on the results of the experiments.



The data in Table 1 refer to a zinc content of 13.5 mg/100 ml and a weight ratio of Al : Zn of 2 : 1. Experiments were carried out under similar conditions with lower and higher Zn concentrations, 2.7-27 mg/100 ml, and the same aluminum content (i.e., 27 mg). The results were quite analogous: within a narrow pH range (5.5-5.8) and with 5 g of ammonium chloride per 100 ml, the reprecipitated precipitate of aluminum hydroxide was free from zinc. Increase in the aluminum concentration to 80 mg of Al^{3+} per 100 ml and simultaneous increase in the zinc concentration to 40 mg/100 ml gave a reprecipitated precipitate of aluminum hydroxide that contained 1-1.25% of the whole of the zinc, even though precipitation was carried out under optimum conditions (pH 5.5-5.8). Entrainment of zinc by the precipitate is so small that one is assured of complete separation in a double reprecipitation.

The adjustment of pH to within the necessary limits was carried out as follows: the solution was neutralized with ammonia until the indicator showed a faint pink coloration, and 1% ammonia solution was then added dropwise until one drop caused the pink tinge to disappear. Under these conditions, at a definite ammonium chloride concentration (5 g/100 ml), the pH was found to be within the range 5.5-5.8; it was always checked electrometrically.

TABLE 1

Results of Experiments on the Separation of Aluminum from Zinc by Precipitation of Aluminum Hydroxide with Ammonia

Amount taken				Amount of zinc found (% on amount taken)					
				First precipitation		Reprecipitation			
Al^{3+} mg	Zn^{2+} mg	NH_4Cl g	pH	Filtrate	Washings	Filtrate	Washings	In reprecipitated precipitate	Total
27.0	13.53	5.11	5.5	87.1	6.2	7.2	Nil	Nil	100.5
27.0	13.53	5.11	5.6	86.0	7.2	7.4	»	»	100.6
27.0	13.53	5.11	5.7	85.9	6.9	7.0	»	»	99.8
27.0	13.53	5.11	5.8	82.2	7.9	9.5	»	»	99.6
27.0	13.53	5.11	5.9	79.4	8.2	12.4	»	1.0	101.0
27.0	13.53	5.11	6.0	80.0	9.4	10.0	»	1.4	100.8
27.0	13.53	5.11	6.1	66.9	6.8	19.8	1.1	5.2	99.8
27.0	13.53	5.11	6.2	58.8	6.0	26.0	1.1	7.3	99.2
27.0	13.53	5.11	6.3	58.2	5.8	21.3	0.9	13.0	99.2
27.0	13.53	5.11	6.6	45.0	6.7	28.7	2.4	18.0	100.8
27.0	13.53	5.11	7.5	59.7	5.9	24.3	2.1	7.5	99.5
27.0	13.53	5.11	8.2	77.2	7.3	11.8	Nil	3.8	100.1
27.0	13.53	5.11	9.1	83.8	6.5	8.2	»	1.8	100.3
27.0	13.53	5.11	9.4	83.8	7.4	8.0	»	1.6	100.8

Separation of Zinc from Iron. Experiments on the separation of zinc from iron were carried out under precisely analogous conditions. As ferric hydroxide is completely precipitated at lower pH values, the pH was varied from 4 to 7.5 in the experiments. The results of some of the experiments are given in Table 2.

TABLE 2

Results of Experiments on the Separation of Zinc from Iron Precipitated with Ammonia

Amount taken				Amount of zinc found (% on amount taken					
				First precipitation		Reprecipitation			
Fe^{3+} (mg)	Zn^{2+} (mg)	NH_4Cl (g)	pH	Filtrate	Washings	Filtrate	Washings	In reprecipitated precipitate	Total
35.6	3.5	5.0	4.0	96.6	2.3	1.1	Nil	Nil	100.0
35.6	3.5	5.0	5.0	88.3	6.5	7.0	»	»	100.0
35.6	3.5	5.0	5.3	96.3	3.3	1.3	»	»	100.9
35.6	3.5	5.0	5.5	93.1	5.4	0.7	»	»	99.2
35.6	3.5	5.0	5.6	86.0	13.5	0.9	»	»	100.4
35.6	3.5	5.0	6.5	52.2	15.2	30.3	0.4	1.6	99.7
35.6	3.5	5.0	7.5	51.6	16.1	24.5	1.7	5.0	89.9

These results are closely in accord with the corresponding results for aluminum. In the precipitation of ferric hydroxide in solutions of pH below 6, complete separation could be obtained. Experiments with an increased amount of zinc for a given iron content gave analogous results.

Separation of Cobalt from Aluminum. Similar experiments were carried out with the object of obtaining more precise information about the conditions for the quantitative separation of cobalt and aluminum. Results of experiments on the effect of the pH of the solution on the entrainment of cobalt by an aluminum hydroxide precipitate for constant concentrations of aluminum, cobalt, and ammonium are given in Table 3.

TABLE 3

Results of Experiments on the Separation of Cobalt from Aluminum Precipitated with Ammonia

Amount taken			pH	Amount of cobalt found (% on amount taken					
				first precipitation		Reprecipitation			
Al^{3+} (mg)	Co^{2+} (mg)	NH_4Cl (g)		Filtrate	Washings	Filtrate	Washings	In reprecipitated precipitate	Total
27.0	3.0	5.05	5.6	93.3	5.0	1.3	Nil	Nil	99.6
27.0	3.0	5.05	5.7	94.0	4.0	1.7	»	»	99.7
27.0	3.0	5.05	5.8	85.7	8.3	6.7	»	»	100.7
27.0	3.0	5.05	6.0	94.3	2.0	4.0	»	»	100.3
27.0	3.0	5.05	6.2	93.3	1.7	2.3	»	1.7	100.0
27.0	3.0	5.05	6.3	91.7	1.7	5.0	»	1.0	99.4
27.0	3.0	5.05	7.4	19.0	15.7	14.3	7.7	44.0	100.7
27.0	3.0	5.05	7.6	20.3	8.7	18.7	11.0	42.0	100.7
27.0	3.0	5.05	8.9	27.7	10.0	31.7	7.7	23.0	100.1
27.0	3.0	5.05	9.2	31.0	10.7	38.7	8.0	11.7	100.1

In general character the dependence on pH is the same as in the case of zinc (Table 1). Complete separation is attained when the precipitation of aluminum hydroxide is carried out from a solution containing 5% of ammonium chloride in the pH range 5.5-6.0. With rise in pH the amount of cobalt coprecipitated with aluminum hydroxide increases still more sharply than in the case of zinc under like conditions. When the excess of ammonia is considerable, the amount of coprecipitated cobalt begins to fall owing to the formation of its ammine.

The essential point is that complete separation of aluminum and cobalt can be attained even when the relative amounts of the ions are unfavorable, cobalt predominating over aluminum. The results are given in Table 4.

Separation of Cobalt from Iron and Aluminum. The above-cited data on the separation of aluminum and cobalt and the analogy with previously cited data on the separation of zinc and iron enabled us to foresee that ferric hydroxide may be separated from cobalt just as completely so long as the pH of the solution during precipitation does not exceed 6.0 and the solution contains not less than 5 g of ammonium chloride per 100 ml. As ferric hydroxide is completely precipitated even at lower pH, it is evident that the pH range in which iron can be quantitatively separated from cobalt can be extended in the direction of more acidic solutions. This is confirmed by experiment.

When iron and aluminum are present simultaneously, the extent to which the pH at which precipitation is carried out can be lowered is limited because of the danger of incomplete precipitation of the aluminum. It may be expected, however, that ferric hydroxide will be a "collector" for aluminum hydroxide and will enable us to lower the pH without any risk of incomplete precipitation of aluminum. This was confirmed by experiment.

TABLE 4

Results of Experiments on the Separation of Cobalt from Aluminum Precipitated with Ammonia

Amount taken				Amount of cobalt found (% on amount taken					
				first precipitation		Reprecipitation			
Al^{3+} (mg)	Co^{2+} (mg)	NH_4Cl (g)	pH	Filtrate	Washings	Filtrate	Washings	In reprecipitated precipitate	Total
27.0	53.9	5.08	5.5	90.9	5.0	4.0	Nil	Nil	99.9
27.0	53.9	5.08	5.5	82.0	6.5	10.7	»	»	99.2
27.0	53.9	5.08	5.6	88.1	6.1	6.5	»	»	100.7
27.0	53.9	5.08	5.6	86.9	5.2	6.4	1.3	»	99.8
27.0	53.9	5.08	5.7	86.4	5.0	6.9	1.1	»	99.4
27.0	53.9	5.08	5.8	85.9	5.0	8.9	Nil	»	99.8
27.0	53.9	5.08	5.8	83.4	2.4	12.3	2.7	»	100.8
27.0	53.9	5.08	5.9	76.4	7.9	12.8	2.4	»	99.5
27.0	53.9	5.08	6.0	70.6	4.9	19.3	1.8	4.1	100.7
27.0	53.9	5.08	6.1	37.5	11.5	39.4	2.4	9.0	99.8

The solution contained 13.3 mg of Al^{3+}, 18.7 mg of Fe^{3+}, 4.27 mg of Co^{2+}, and 5.26 g ammonium chloride. Not only was the cobalt entrained by the precipitate determined, but also the completeness of the precipitation of aluminum and iron. The results of the experiments are given in Table 5.

As can be seen from Table 5, aluminum was completely precipitated with ferric hydroxide in spite of the relatively low pH of the solution during precipitation: the ferric hydroxide played the part of a "collector".

2. Behavior of Zinc and Cobalt in the Precipitation of Aluminum and Iron by the so-called "Acetate-Hydrolysis" Method

First of all we made a more precise examination of the relationship between the completeness of precipitation of basic aluminum acetate and the pH of the solution. For this purpose we took 100 ml of solution containing not only aluminum chloride but also hydrochloric acid, and added ammonia solution until a turbidity appeared, which was removed by addition of 1-2 drops of dilute hydrochloric acid. The solution was heated to the boil and diluted with boiling water to about 300 ml, after which 10 ml of N acetic acid and 1-6 g of solid ammonium acetate were added. The hot solution was allowed to stand for 10-15 minutes, and the precipitate was then filtered off and washed with 1% ammonium acetate solution. The precipitate was dried, calcined, and weighed. The pH of the main filtrate was determined electrometrically. The results are given in Table 6.

As will be seen from Table 6, complete precipitation of aluminum occurs only in the pH range 7.5-7.8, i.e., only when basic aluminum acetate is already being transformed into aluminum hydroxide [13, 14].

In order to find the behavior of zinc in the separation of aluminum by the above-described method, experiments were carried out in the following manner. A solution of the radioactive isotope of zinc was introduced into a solution containing definite amounts of aluminum and zinc chlorides; the solution was made up to 100 ml, and the activity of this original solution was measured. Precipitation of basic aluminum acetate was then carried out as described above. The washed precipitate was dissolved in dilute hydrochloric acid, and basic aluminum acetate was reprecipitated from the resulting solution in the same way. In both precipitations the filtrates and washings were combined. As we were interested not only in the completeness of separation of zinc, but also in the completeness of the separation of aluminum, each of the solutions, after precipitation and after reprecipitation was evaporated to low bulk and was treated with ammonia to precipitate any residual aluminum. These supplementary precipitates of aluminum hydroxide were filtered off, washed, calcined, weighed.

TABLE 5

Results of Experiments on the Separation of Cobalt from Iron and Aluminum

pH	Amount of cobalt found (% on amount taken)						Amount of $Al_2O_3 + Fe_2O_3$ Found (% on amount taken)
	First precipitation		Reprecipitation		In reprecipitated precipitate	Total	
	Filtrate	Washings	Filtrate	Washings			
5.2	91.0	2.0	3.0	3.1	Nil	99.1	100.02
5.3	95.9	3.3	0.5		»	99.7	99.96
5.3	95.9	2.4	0.5	0.5	»	99.3	99.98
5.3	96.2	2.1	2.4		»	100.7	100.00
5.5	70.3	5.9	20.3	4.5	»	101.0	—
5.6	74.2	6.6	16.1	3.0	»	99.9	—
5.7	80.4	7.0	8.6	3.6	»	99.6	—
5.8	89.3	4.2	6.1		»	99.6	—
5.9	87.8	5.8	3.9	2.1	»	99.6	—
6.0	57.6	4.2	35.3	0.6	2.4	100.1	—
6.2	51.2	5.9	17.6	3.3	22.0	100.0	—
6.4	37.2	4.8	28.7	5.2	23.0	98.9	—

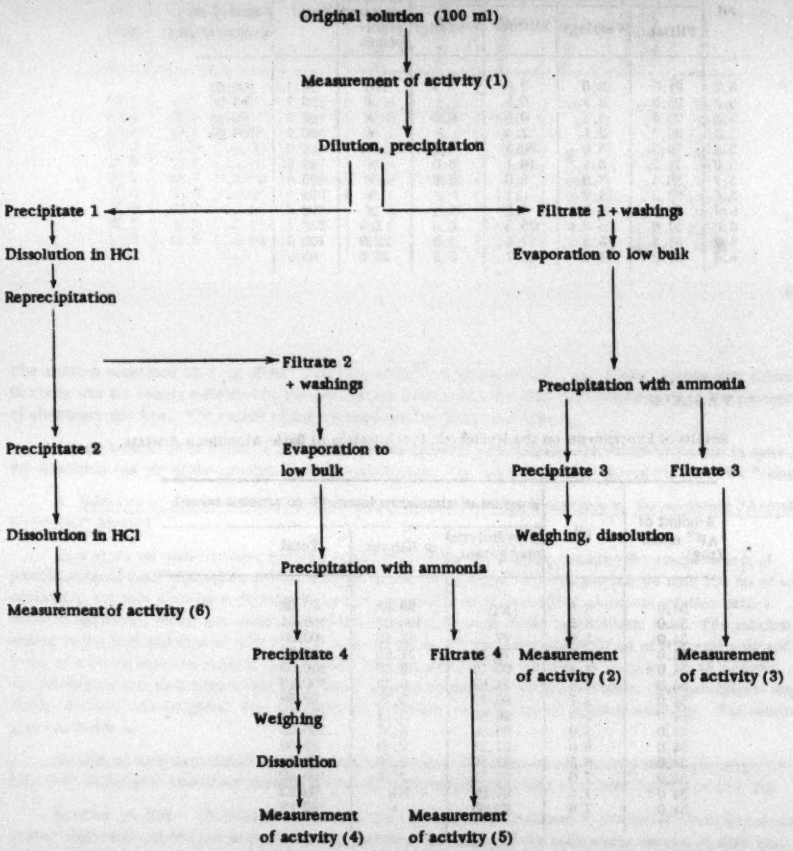
TABLE 6

Results of Experiments on the Hydrolytic Precipitation of Basic Aluminum Acetate

Amount of Al^{3+} taken (mg)	pH	Amount of aluminum found (% on amount taken)		
		in hydrolytic precipitate	in filtrate	Total
54.0	4.8	Nil	99.98	99.98
54.0	4.9	»	100.01	100.01
54.0	5.0	27.2	73.10	100.30
54.0	5.2	78.3	21.67	99.67
54.0	5.4	90.70	9.30	100.00
54.0	5.5	94.88	5.22	100.10
54.0	5.7	96.72	3.26	99.98
54.0	5.8	96.66	3.47	100.13
54.0	5.9	96.86	3.37	100.23
54.0	6.0	97.28	2.40	99.96
54.0	6.5	97.56	2.40	99.96
54.0	7.0	97.72	2.28	100.00
54.0	7.5	99.82	Nil	99.82
54.0	7.8	99.88	»	99.88

* The aluminum contents of the filtrates were determined by means of aluminum, either gravimetrically (for high contents) or colorimetrically.

The alumina precipitates were dissolved, and the activities of the resulting solutions were measured. The activities of both filtrates from the precipitation of aluminum were measured, as also was that of the solution obtained by dissolving the main precipitate of basic aluminum acetate in dilute hydrochloric acid. The following scheme will make the procedure clear.



By adding activities (2+3 and 4+5), we are able to determine the behavior of zinc in the first and second precipitations of basic acetate. Measurement of activity (6) enables us to calculate the amount of zinc entrained by the reprecipitated basic aluminum acetate. Measurements (2) and (4) enable us to determine the amount of zinc entrained in the supplementary precipitation of aluminum hydroxide. Finally, the weights of the precipitates (3) and (4) characterize the incompleteness of the precipitation of aluminum under the given experimental conditions. Tables 7 and 8 give the results of experiments on the separation of aluminum and zinc in accordance with the scheme described.

TABLE 7

Results of Experiments on the Separation of Zinc and Aluminum by the Acetate-hydrolysis Method

Experiment	Amount taken		pH	Amount of zinc found (% on amount taken			
	Al^{3+} (mg)	Zn^{2+} (mg)		Filtrate 1	Filtrate 2	In reprecipitated precipitate	Total
1	28.58	28.21	5.4	95.22	4.28	Nil	99.50
2	28.58	28.21	5.5	95.75	4.99	»	100.74
3	28.58	28.21	5.6	94.06	5.94	»	100.00
4	28.58	28.21	5.7	95.24	4.97	»	100.21
5	28.58	28.21	5.8	94.90	4.90	»	99.80
6	28.58	28.21	5.9	94.14	5.86	»	100.00
7	28.58	28.21	6.0	92.70	7.60	»	100.30
8	28.58	28.21	6.4	83.48	14.26	2.65	100.39

TABLE 8

Aluminum Contents of Filtrates and Losses of Zinc in Supplementary Precipitations of Aluminum Hydroxide

Experiment	Amount of aluminum found (% on initial content)		Amount of zinc entrained in supplementary precipitation of aluminum (% on total zinc content)	
	Filtrate 1	Filtrate 2	precipitate from first filtrate	precipitate from second filtrate
1	6.57	5.38	4.15	1.38
2	5.21	5.16	3.85	1.84
3	5.13	4.37	2.56	2.46
4	2.31	2.41	3.74	1.02
5	—	—	3.10	1.70
6	—	—	3.24	2.41
7	—	—	3.12	1.54
8	—	—	3.48	2.94

As will be seen from Tables 7 and 8, zinc remains completely in solution when the precipitation of the basic aluminum acetate is carried out at pH below 6. Under these conditions, however, some aluminum also remains in solution, and in its complete precipitation there is a considerable loss of zinc, up to 5-6% of its total content. Experiments with different proportions of aluminum and zinc (increase of the amount of aluminum to 57 mg and variation of the weight ratio of Al^{3+} to Zn^{2+} from 10:1 to 1:2) gave completely analogous results.

Above, we pointed out the increase in the completeness of precipitation of aluminum by ammonia observed by us even at low pH when iron was present simultaneously. It was of interest to determine whether basic ferric acetate could act as a "collector" in the same way and whether completeness of separation of aluminum and zinc could be achieved by the introduction of iron. The procedure for the precipitation and reprecipitation of basic acetates was as described above. The results are given in Table 9.

TABLE 9

Results of Experiments on the Separation of Aluminum and Zinc in Presence of Iron

Amount taken			pH	Amount of $Al_2O_3+Fe_2O_3$ found (% on total amount)				Zinc found in reprecipitated precipitate
Al^{3+} (mg)	Fe^{3+} (mg)	Zn^{2+} (mg)		In reprecipitated precipitate	Filtrate 1	Filtrate 2		
28.58	9.72	42.31	5.4	95.58	2.30	2.40	100.28	Nil
28.58	9.72	42.31	5.6	95.72	1.90	3.18	100.80	»
28.58	9.72	42.31	5.5	95.67	2.50	2.28	100.45	»
14.25	19.44	42.31	5.4	99.89	Nil	Nil	99.89	»
14.25	19.44	42.31	5.5	100.47	»	»	100.47	»
14.25	19.44	42.31	5.6	99.92	»	»	99.92	»
14.25	19.44	42.31	5.7	100.00	»	»	100.00	»
14.25	19.44	42.31	5.8	99.83	»	»	99.83	»

The data in Table 9, which have been confirmed by many experiments, showed that basic ferric acetate, and probably also ferric hydroxide formed at pH below 5.8, is a "collector" for aluminum, and the presence of iron in an amount exceeding that of aluminum ensures complete precipitation of aluminum and its complete separation from zinc.

Completely analogous results were obtained for the separation of aluminum from cobalt. When the precipitation of basic aluminum acetates by the above-described method was carried out at pH not above 6, cobalt remained completely in solution irrespective of the proportions of aluminum to cobalt, but in the supplementary precipitation of aluminum from the filtrates with ammonia up to 5% of the total amount of cobalt was entrained in the aluminum hydroxide precipitates. It is interesting that, in this case also, iron acted as a "collector" for aluminum, and when iron predominated over aluminum it was possible to separate the latter from cobalt quantitatively. Thus, in experiments in which the amounts of Al^{3+}, Fe^{3+}, and Co^{2+} were 28.58, 18.88, and 38.4 mg respectively, part of the aluminum remained unprecipitated, but when the amounts of these ions were 14.29, 37.76, and 38.40 mg respectively, aluminum passed completely into the precipitate and cobalt passed completely into the solution.

3. Behavior of Zinc and Cobalt in the Precipitation of Aluminum and Iron with Pyridine

The following procedure was adopted: 100 ml of solution containing the required amounts of the various salts was neutralized with ammonia until a turbidity appeared, and this was removed by addition of a few drops of dilute hydrochloric acid. Ammonium chloride (10 g) was added, the solution was heated, and the hydroxide was precipitated by slow addition of 20% pyridine solution until a faint odor of pyridine remained. The solution was stirred, 20 ml of pyridine solution was added, and the precipitate was allowed to settle and was then filtered off and washed with a 3% solution of ammonium chloride containing a little pyridine. The precipitate was dissolved in hydrochloric acid and was reprecipitated in accordance with the same procedure. In both cases the washings were collected separately. The distribution of zinc between precipitate and solutions was determined by introducing the radioactive isotope into the original solution and measuring the activities of the solutions and redissolved precipitates. The results of the experiments on the separation of aluminum and zinc are given in Table 10.

As will be seen from Table 10, the best separation is attained at pH 6-6.5; on the other hand, in the pH range that is favorable for separation by means of ammonia or hydrolysis (5.5-5.9), separation is incomplete. It was not possible to raise the pH above 6.5 by means of pyridine. Reduction of the ammonium chloride concentration below 8g/100 ml resulted in considerable coprecipitation of zinc with aluminum hydroxide. Aluminum and iron are completely precipitated when the above-described conditions are observed.

TABLE 10

Results of Experiments on the Separation of Aluminum and Zinc by Pyridine

Amount taken				Amount of zinc found (% on amount taken					
				First precipitation		Reprecipitation			
Al^{3+} (mg)	Zn^{2+} (mg)	NH_4Cl (g)	pH	Filtrate	Washings	Filtrate	Washings	In reprecipitated precipitate	Total
28.58	28.33	10	5.5	85.02	2.13	5.87	2.42	4.52	99.96
28.58	28.33	10	5.6	85.79	2.89	5.95	1.87	3.37	99.87
28.58	28.33	10	5.8	89.13	2.63	4.32	1.18	3.14	100.40
28.58	28.33	10	5.9	90.20	2.75	4.18	1.28	1.62	100.03
28.58	28.33	10	6.0	92.15	2.35	3.81	1.66	Nil	100.00
28.58	28.33	10	6.2	92.91	2.78	4.68	Nil	»	100.37
28.58	28.33	10	6.3	92.80	3.13	3.67	»	»	99.60
28.58	28.33	10	6.4	93.11	3.37	3.47	»	»	99.65
28.58	28.33	10	6.5	93.10	2.75	4.15	»	»	100.00

Similar results were obtained for the separation of aluminum and also of aluminum and iron, from cobalt. In this case also, complete separation is attained when the pH of the solution is above 6. The ammonium chloride concentration is not of particular importance and can be considerably reduced (to 2 g/100 ml). When the cobalt content is low, it is not necessary to reprecipitate the precipitate.

SUMMARY

1. A study was made of the conditions ensuring complete separation of zinc and cobalt from aluminum and iron, the latter being precipitated with ammonia, in the form of basic acetates, or with pyridine.

2. It was shown that, for the first of these methods, complete separation of both zinc and cobalt from aluminum and iron is attained only within a narrow pH range, 5.5-5.9, and it is necessary that not less than 8% of ammonium salt should be present. Under these conditions separation is attained irrespective of the relative amounts of the ions to be separated. It was shown that ferric hydroxide is a "collector" for aluminum hydroxide and presence of iron in the solution permits complete precipitation of aluminum at relatively low pH.

3. The "acetate-hydrolysis" method is unsuitable when zinc or cobalt is accompanied only by aluminum, for the latter very incompletely precipitated. However, the presence of iron in amounts exceeding the amount of aluminum removes this defect of the method. Precipitation of ferric and aluminum hydroxides with excess of pyridine gives excellent separation of zinc and cobalt from aluminum and iron.

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ORGANIC AND BIOLOGICAL CHEMISTRY

CONDENSATION OF 2-CHLOROVINYL KETONES WITH BENZENE AND ITS HOMOLOGS

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We have shown previously that 2-chlorovinyl ketones react readily with phenols [1, 2] and their ethers [3] with formation of the corresponding styryl ketones. The present paper is concerned with the study of the condensation of 2-chlorovinyl ketones with benzene and its homologs. It was found that the condensation of 2-chlorovinyl ketones even with active benzene homologs does not go in presence of stannic chloride, which is an active catalyst, as shown for the case of phenol ethers [3]. Even in presence of aluminum chloride in complete absence of moisture, the desired results were not obtained. However, by the use of moist m-xylene in reaction with 4-chloro-3-buten-2-one in presence of aluminum chloride, 4-(2, 4-xylyl)-3-buten-2-one was obtained in 43% yield.

In the course of the investigation it was found that the condensation of 2-chlorovinyl ketones with benzene and its homologs proceeds more satisfactorily in presence of aluminum chloride in a strong current of moist hydrogen chloride. The necessity for moisture is worthy of attention; almost no reaction occurs in a stream of dry hydrogen chloride.

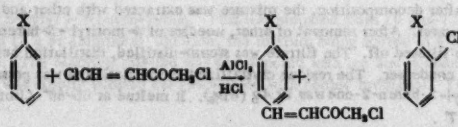
$$ArH + ClCH = CHCOR \xrightarrow[HCl]{AlCl_3} ArCH = CHCOR$$

I) $R = CH_3-$; $Ar = m\text{-}(CH_3)_2C_6H_3-$; $p\text{-}(CH_3)_2C_6H_3-$; $symm\text{-}(CH_3)_3C_6H_2-$

II) $R = C_6H_5-$; $Ar = m\text{-}(CH_3)_2C_6H_3-$; $symm\text{-}(CH_3)_3C_6H_2-$

III) $R = CH_2Cl-$; $Ar = C_6H_5-$, $CH_3C_6H_4-$, $m\text{-}(CH_3)_2C_6H_3-$, $p\text{-}(CH_3)_2C_6H_3$; ClC_6H_4-

It should be noted that not all 2-chlorovinyl ketones react equally readily. It was found that 4-chloro-3-buten-2-one reacts readily with comparatively active benzene homologs such as mesitylene and m-xylene. With p-xylene it reacts feebly, 4-(2, 5-xylyl)-2-buten-2-one being formed in only 20% yield, and with toluene and benzene it does not react at all under these conditions. 3-Chloroacrylophenone also reacts readily with mesitylene and with m-xylene, but with toluene it gives a negligible yield. The most reactive vinyl ketone was found to be 1,4-dichloro-3-buten-2-one, which reacts readily not only with m- and p-xylenes, but also with toluene and with benzene, giving the previously inaccessible 4-aryl-1-chloro-3-buten-2-ones in high yield (50-79%). Reaction proceeds even with chlorobenzene, which by condensation with 1, 4-dichloro-3-buten-2-one gives a mixture of o- and p-isomers.



$X = CH_3-$, Cl—.

When the mixture is oxidized with potassium permanganate, phthalic and terephthalic acids can be iso-

lated and identified in the first case, and o- and p-chlorobenzoic acids in the second.

The styryl ketones that we synthesized from 2-chlorovinyl ketones corresponded in properties and constants with known styryl ketones obtained by the condensation of the corresponding aromatic aldehydes with acetone and acetophenone. Treatment of 4-(2,4-xylyl)-3-buten-2-one with iodine in alkaline medium gave the already known 2, 4-dimethylcinnamic acid. The same 2, 4-dimethylcinnamic acid was isolated also in the oxidation with stannic chloride of 1-chloro-4-(2, 4-xylyl)-3-buten-2-one, obtained by reaction between 1, 4-dichloro-3-buten-2-one and m-xylene.

EXPERIMENTAL

4-(2, 4-Xylyl)-3-buten-2-one. a) A powerful current of moist hydrogen chloride was passed through an ice-cooled solution of 15 g of 4-chloro-3-buten-2-one in 30.5 g of m-xylene for ten minutes. Aluminum chloride (19.5 g) was then added in portions with vigorous agitation and continued passage of the powerful current of hydrogen chloride. When the whole of the aluminum chloride had been added, cooling was discontinued. The reaction mixture was stirred in the stream of hydrogen chloride until a dark-red complex was precipitated (3-4 hours). After 20-30 minutes the reaction mixture was decomposed with a mixture of ice and concentrated hydrochloric acid. The mixture was extracted with ether, and the ether extracts were washed several times with water and dried over calcium chloride. Distillation gave 16 g (64.2%) of 4-(2, 4-xylyl)-3-buten-2-one, b.p. 145-146° (8 mm). The literature [4] gives b.p. 145-148° (10 mm). The semicarbazone, prepared in the usual way, had m.p. 226-228° (from alcohol); the literature [4] gives m.p. 227°.

4-(2, 4-Xylyl)-3-buten-2-one is a colorless viscous liquid of pleasant odor. It crystallizes when cooled upon scratching of the sides of the flask with a glass rod; m.p. 32°. It is readily soluble in the usual organic solvents.

b) Aluminum chloride (19.5 g) was added in portions to a cooled stirred solution of 15 g of 4-chloro-3-buten-2-one in 30.5 g of moist m-xylene. Stirring was continued at room temperature for four hours. Decomposition and treatment as given in Experiment (a) gave 11 g (43.6%) of 4-(2, 4-xylyl)-3-buten-2-one, b.p. 139-142° (5-6 mm). Semicarbazone: m.p. 227°, undepressed by admixture with sample obtained in the previous experiment.

The iodoform reaction was carried out with 4-(2, 4-xylyl)-3-buten-2-one in the usual way; it gave 2, 4-dimethylcinnamic acid, m.p. 180° (from benzene) (the literature [4] gives 181°).

Found %: C 75.29; H 7.01. $C_{11}H_{12}O_2$. Calculated %: C 75.01; H 6.86.

4-(2, 5-Xylyl)-3-buten-2-one. The procedure was as in Experiment (a), the reactants being 4-chloro-3-buten-2-one (6 g), p-xylene (13 g), and aluminum chloride (7.7 g). The mixture was stirred in a vigorous stream of hydrogen chloride for five hours. After the dark-red complex had been precipitated, the reaction mixture was heated for 30 minutes at 35-37°. The product was 2 g (20%) of 4-(2, 5-xylyl)-3-buten-2-one, b.p. 130° (4-4.5 mm); the literature [5] gives 154-156° (15 mm). The semicarbazone was prepared in the usual way; m.p. 201-202° (the literature [5] gives 204°).

4-(2, 5-Xylyl)-3-buten-2-one is a colorless viscous liquid of pleasant odor, readily soluble in the usual organic solvents.

4-Mesityl-3-buten-2-one. This was prepared in a similar way from 14 g of 4-chloro-3-buten-2-one, 30.6 g of mesitylene, and 18.1 g of aluminum chloride. The mixture was stirred in a stream of moist hydrogen chloride for three hours. After decomposition, the mixture was extracted with ether and the ether extracts were washed several times with water. After removal of ether, needles of 4-mesityl-3-buten-2-one came down from the residue, and these were filtered off. The filtrate was steam-distilled, distillation being interrupted as soon as crystals appeared in the condenser. The residue crystallized in the flask and was pressed off on a porous plate. The total yield of 4-mesityl-3-buten-2-one was 10.4 g (61%). It melted at 65-66° (from aqueous alcohol); the literature [6] gives m.p. 67°.

Found %: C 83.18; H 8.65. $C_{13}H_{16}O$. Calculated %: C 82.98; H 8.55. The semicarbazone was prepared in the usual way; m.p. 190-191° (from alcohol). Found %: N 16.87; 16.82. $C_{14}H_{19}ON_3$. Calculated %: N 17.13.

2,4,6-Trimethylchalcone. This was prepared similarly from 10 g of 3-chloroacrylophenone [7], 15 g of mesitylene, and 8.1 g of aluminum chloride. The mixture was stirred in a stream of hydrogen chloride until the complex was precipitated (4 hours). The mixture was decomposed and then extracted with benzene. The benzene extracts were washed several times with water and then steam-distilled. After the removal of benzene and mesitylene, distillation was discontinued. The residue crystallized and was filtered, the crystals being well pressed off on the filter. The yield was 8.5 g (56.6%); m.p. 95° (from diluted alcohol) (the literature [6] gives 96°).

Found %: C 86.20; H 7.20. $C_{18}H_{18}O$. Calculated %: C 86.40; H 7.25.

2,4,6-Trimethylchalcone forms needles, readily soluble in ether and benzene and moderately soluble in alcohol. Its semicarbazone melts at 188° (from alcohol).

Found %: C 74.10, 73.93; H 6.83, 6.81; N 13.70, 13.72. $C_{19}H_{21}ON_3$. Calculated %: C 74.23; H 6.88; N 13.67.

1-Chloro-4-phenyl-3-buten-2-one. This was prepared similarly from 10 g of 1,4-dichloro-3-buten-2-one, 50 ml of benzene, and 10 g of aluminum chloride, the mixture being vigorously agitated in a strong current of hydrogen chloride for 4.5-5 hours. After precipitation of the dark-red complex, the mixture was heated for 30 minutes at 40-45°. The mixture was decomposed and extracted with ether. Vacuum distillation gave 10.25 g (79%) of 1-chloro-4-phenyl-3-buten-2-one, b.p. 138-139° (5 mm), m.p. 62° (from aqueous alcohol).

Found %: C 66.10; H 5.09. $C_{10}H_9OCl$. Calculated %: C 66.49; H 5.23.

1-Chloro-4-phenyl-3-buten-2-one forms colorless needles, readily soluble in ether, chloroform, and acetone and moderately soluble in cold benzene and petroleum ether.

Boiling of 1-chloro-4-phenyl-3-buten-2-one in m-xylene solution with excess of stannic chloride for many hours gave 2,4-dimethylcinnamic acid, m.p. 179°; the literature [4] gives 181°. In admixture with the sample obtained previously there was no depression of melting point.

1-Chloro-4-o-tolyl- and 1-Chloro-4-p-tolyl-3-buten-2-ones. These were prepared similarly from 15 g of 1,4-dichloro-3-buten-2-one, 30 g of toluene, and 15 g of aluminum chloride, the mixture being vigorously agitated in a strong current of hydrogen chloride for two hours. The reaction mixture was decomposed with ice and concentrated hydrochloric acid. The precipitate formed was rapidly filtered off, washed with ice water, and well pressed off. A mixture of o- and p-isomers was obtained; yield 17.5 g (83.7%); m.p. of mixture 49-52°.

Found %: C 67.90; 67.62; H 5.63; 5.69; Cl 18.67. $C_{11}H_{11}OCl$. Calculated %: C 67.89; H 5.75; Cl 18.22.

Oxidation of the mixture with potassium permanganate in 5% sodium carbonate solution gave a mixture of phthalic and terephthalic acids, which we succeeded in separating by fractional crystallization from alcohol. Terephthalic acid does not melt; its dimethyl ester, prepared by boiling the acid in methanol in presence of concentrated sulfuric acid, melted at 137° (the literature [8] gives 140°); a mixture test with a known sample showed no depression. Phthalic acid melted at 189° (rapid heating), and its anhydride at 126° (the literature [9] gives 128°); a mixture test with a known sample showed no depression.

1-Chloro-4-(2,5-xylyl)-3-buten-2-one. This was prepared from 10 g of 1,4-dichloro-3-buten-2-one, 22.8 g of p-xylene, and 10 g of aluminum chloride, the mixture being stirred in a powerful current of hydrogen chloride for three hours. The reaction mixture was decomposed with ice and concentrated hydrochloric acid; the precipitate formed was rapidly filtered off and washed with cooled methanol. Yield 10.8 g (74.8%); m.p. 98-100° (from alcohol).

Found %: C 68.76; 68.75; H 6.22, 6.36; Cl 16.76; 17.10. $C_{12}H_{13}OCl$. Calculated %: C 69.04; H 6.28; Cl 16.97.

1-Chloro-4-(2,5-xylyl)-3-buten-2-one forms colorless needles which can be readily crystallized from aqueous alcohol.

1-Chloro-4-o-chlorophenyl- and 1-Chloro-4-p-chlorophenyl-3-buten-2-ones. These were prepared similarly from 10 g of 1,4-dichloro-3-buten-2-one, 20 g of chlorobenzene, and 10 g of aluminum chloride, the mixture being stirred at room temperature in a powerful current of hydrogen chloride for ten hours. The reaction mixture was decomposed with ice and hydrochloric acid and extracted with ether. Unchanged chlorobenzene and ketone were distilled off with steam, and the residue was distilled off with superheated steam. The product was 1.65 g (10.7%) of a mixture of o- and p-isomers; m.p. of mixture 70-80°.

Found: %: C 55.84; 56.02; H 3.60; 3.38; Cl 33.48; 32.95. $C_{10}H_8OCl_2$. Calculated %: C 55.84; H 3.75; Cl 32.96.

Oxidation of the mixture with potassium permanganate in 5% sodium carbonate solution gave a mixture of o- and p-chlorobenzoic acids, which were separated by fractional crystallization from water. p-Chlorobenzoic acid melted at 238°; the literature [10] gives m.p. 236-237°. o-Chlorobenzoic acid melted at 136°; the literature [11] gives m.p. 137°. Mixture tests with known samples showed no depression.

SUMMARY

1. A new method was developed for the synthesis of styryl ketones. It consists in the condensation of 2-chlorovinyl ketones with aromatic hydrocarbons in presence of aluminum chloride and moist hydrogen chloride.

2. It was shown that 1,4-dichloro-3-buten-2-one is extremely reactive in this reaction.

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ACTION OF CHLORINE ON UNSATURATED POLYCHLORO COMPOUNDS IN AN ACID MEDIUM

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As we have shown previously [1], compounds of structure

$CCl_2=CH-CH_2X$ in which X=OCH_3, $N(C_2H_5)_2$, NO_2, etc.,

combine smoothly with chlorine when the substituent X is an electron acceptor, whereas in cases in which this substituent is an electron donor, not only addition occurs, but also replacement of hydrogen by chlorine.

It was considered that replacement of allyl hydrogen occurred, but it has now been found that treatment of 1, 1-dichloro-3-methoxypropene with chlorine gives mainly a product in which the methoxy group is chlorinated:

$$CCl_2=CHCH_2OCH_3+Cl_2\rightarrow CCl_2CHClCH_2OCH_2Cl.$$

The structure of this product was proved by its conversion into 2, 3, 3, 3-tetrachloro-1-propanol by the action of methanol in presence of hydrochloric acid. We also synthesized 1, 1, 1, 2-tetrachloro-3-(chloromethoxy) propane by the chloromethylation of 2, 3, 3, 3-tetrachloro-1-propanol. When compounds of the above structure containing an electron-donating substituent (OCH_3, $N(C_2H_5)_2$) are treated with chlorine in presence of hydrogen chloride, the substitution reaction predominates [1].

It was further shown [2] that compounds containing the $CCl_2=CH$ group react with chlorine in a H_2SO_4 medium by "conjugated addition" with formation of α-chloro carboxylic acids in accordance with the scheme:

$$RCH=CCl_2+Cl_2\xrightarrow{H_2SO_4}[RCHCl-CCl_2OSO_3H]\xrightarrow{H_2O}RCHClCOOH.$$

In this way good yields were obtained of α-chloro carboxylic, α,ω-dichloro carboxylic, and α-chloro dicarboxylic acids from compounds of the type $CH_3(CH_2)_nCH=CCl_2$, $Cl(CH_2)_nCH=CCl_2$ and $HOOC(CH_2)_nCH=CCl_2$, respectively.

In the present investigation we have shown that the suppression of substitution on saturated carbon atoms of compounds of structure $CCl_2=CH(CH_2)_nX$ in chlorine treatments in presence of hydrogen chloride is of great general significance. For example, when 1, 1, 5-trichloro-1-pentene, 6, 6-dichloro-5-hexenenitrile, and 8, 8-dichloro-7-octenoic acid were treated with chlorine in chloroform at 0-15°, reaction went with brisk evolution of hydrogen chloride and formation of a mixture of chlorination products. In presence of hydrogen chloride these unsaturated compounds smoothly combined with chlorine at the double bond with formation in good yield of 1, 1, 1, 2, 5-pentachloropentane, 5, 6, 6, 6-tetrachlorohexanoic acid, and 7, 8, 8, 8-tetrachlorooctanoic acid, respectively.

In order to determine the relationship between the strength of an acid and the effect of the acid on the reaction between chlorine and compounds containing the $CCl_2=CH$ group, a study was made of the reaction of 1, 1, 5-trichloro-1-pentene and chlorine in media of glacial acetic acid, 90% phosphoric acid, concentrated sulfuric acid, and 70% perchloric acid at 0-15° without irradiation. It was found that conjugated addition of

chlorine with formation (after treatment with water) of 2,5-dichlorovaleric acid occurred only in media of sulfuric (concentrated) and perchloric acids. In 70% sulfuric acid, as in presence of hydrogen chloride, addition of chlorine at the double bond occurred without appreciable substitution at saturated carbon atoms. In this respect there is a definite difference in behavior between dichlorovinyl compounds and olefins in these reactions. As is well known, olefins react with chlorine by "conjugated addition" not only in media of strong mineral acids, but also in other media (see, for example, [3,4]).

The preparation of α-chloro carboxylic acids by the action of chlorine on dichlorovinyl compounds in concentrated sulfuric acid is carried out under mild conditions, so that it is possible to prepare α-chloro carboxylic acids containing various substituents. In particular, in this paper we describe the action of chlorine on 1,1,5,5,5-pentachloro-1-pentene in concentrated sulfuric acid, in which a trichloromethyl group is preserved and 2,5,5,5-tetrachlorovaleric acid is obtained.

There are as yet no experimental data on the orienting effect of the trichloromethyl group on electrophilic addition at the double bond of a compound containing the grouping $CCl_3C{=}C$. Attempts to investigate the reaction between hydrogen bromide and 3,3,3-trichloropropene with this object were not successful, since reaction occurred only in presence of aluminum chloride, which isomerized the original compound into 1,1,3-trichloropropene [5] (compare [13]), or in presence of benzoyl peroxide, in which case reaction occurred with isomerization into an intermediate radical [6]. It was therefore of interest to study the electrophilic conjugated addition of chlorine to 3,3,3-trichloropropene.

According to Titov and Maklyaev [3], addition of chlorine to propene in a medium of acetic, formic, or benzenesulfonic acid results in the formation of a compound of the formula:

$$CH_3-\underset{\displaystyle OX}{\underset{|}{CH}}-CH_2Cl,$$ in which $X = CH_3CO-$, $HCO-$, $C_6H_5SO_2-$,

so that the reaction is subject to the usual rules of electrophilic addition. When chlorine reacted with 3,3,3-trichloropropene in concentrated sulfuric acid or glacial acetic acid, in addition to 1,1,1,2,3-pentachloropropane, 2,3,3,3-tetrachloro-1-propanol was obtained in form of its sulfate or acetate, respectively. Hydrolysis of these esters gave 2,3,3,3-tetrachloro-1-propanol, which was found to be identical with the substance obtained as follows:

$$CCl_3CH=CH_2 + CH_3COONa \xrightarrow{CH_3COOH} CCl_2=CH-CH_2OCOCH_3 \xrightarrow[HCl]{CH_3OH}$$
$$\rightarrow CCl_2=CH-CH_2OH \xrightarrow[HCl]{Cl_2} CCl_3CHClCH_2OH.$$

It was thus shown that the trichloromethyl group in 3,3,3-trichloropropene has an orienting effect in the direction opposite to that of the methyl group in propene. This result confirms the view of the electron-accepting character of the trichloromethyl group formed by two of the authors of this paper and Zakharkin [7] on the basis of a study of the dissociation constants of a series of acids of structure: $CCl_3(CH_2)_nCOOH$.

EXPERIMENTAL

Action of Chlorine on 1,1,5-Trichloro-1-pentene in Hydrochloric Acid. Chlorine and hydrogen chloride were passed through a solution of 26 g of 1,1,5-trichloro-1-pentene in 15 ml of ether and 15 ml of saturated aqueous hydrogen chloride until no further reaction occurred. The mixture was diluted with water, and the organic layer was separated, washed with water, and dried over calcium chloride. Distillation gave 29 g (81%) of 1,1,1,2,5-pentachloropentane, b.p. 92-93° (2.5 mm); n_D^{20} 1.5104; d_4^{20} 1.4815; found MR 49.37; calculated MR 49.62.

For 1,1,1,2,5-pentachloropentane the literature [8] gives b.p. 121-122° (12 mm); n_D^{20} 1.5135; d_4^{20} 1.4807. The structure of 1,1,1,2,5-pentachloropentane was proved by its hydrolysis with nitric acid to 2,5-dichlo-

rovaleric acid [9].

Action of Chlorine on 6,6-Dichloro-5-hexenenitrile. The chlorine treatment was carried out as in the preceding experiment. When reaction was complete, one volume of the reaction mixture was diluted with one volume of water and two volumes of acetic acid, and the mixture was boiled for six hours in order to hydrolyze the reaction product. A high yield (about 80%) of 5,6,6,6-tetrachlorohexanoic acid, m.p. 47-48° (from petroleum ether), was obtained.

Found %: C 28.51; 28.37; H 3.23; 3.14. $C_6H_8Cl_4O_2$. Calculated %: C 28.38; H 3.17.

Action of Chlorine on 8,8-Dichloro-7-octenoic Acid. A mixture of 6 g of 8,8-dichloro-7-octenoic acid, 6 ml of ether, and 6 ml of hydrochloric acid was saturated with hydrogen chloride and chlorine. The usual treatment gave 8 g (99%) of 7,8,8,8-tetrachlorooctanoic acid, b.p. 158-160° (1 mm) and n_D^{20} 1.5018.

Found %: C 34.28; 34.20; H 4.25; 4.08 $C_8H_{12}Cl_4O_2$. Calculated %: C 34.07; H 4.29.

Hydrolysis of this acid with concentrated nitric acid gave 2-chlorooctanedioic acid, m.p. 98-99° (from chloroform). A mixture of this acid and the substance obtained as follows:

$$CCl_2=CH(CH_2)_5COOH + Cl_2 \xrightarrow{H_2SO_4} HOOCCH(Cl)(CH_2)_5COOH$$

shows no depression of melting point [2].

Action of Chlorine on 1,1,5-Trichloro-1-pentene in Phosphoric Acid. Chlorine was passed at 0-10° through a vigorously stirred mixture of 18 g of 1,1,5-trichloro-1-pentene and 20 g of 90% phosphoric acid until evolution of hydrogen chloride ceased. Treatment of the reaction mixture gave only polychloro hydrocarbons.

Action of Chlorine on 1,1,5-Trichloro-1-pentene in Perchloric Acid. Chlorine was passed at 30° through a mixture of 18 g of 1,1,5-trichloro-1-pentene and 25 g of 70% perchloric acid until evolution of hydrogen chloride ceased. The mixture was then heated in a water bath for two hours. The mixture was diluted with water, the organic layer was separated, and the acid products were removed by washing with a solution of sodium hydroxide. Acidification of the alkaline extract gave 6.5 g (36%) of 2,5-dichlorovaleric acid, b.p. 105-108° (1 mm); n_D^{20} 1.4859; d_4^{20} 1.3440. The literature [9] gives b.p. 129-131° (5 mm); n_D^{20} 1.3421.

The neutral products were not investigated because of the risk of explosion.

Action of Chlorine on 1,1,5,5,5-Pentachloro-1-pentene in Sulfuric Acid. The pentachloropentene was prepared, as previously described [10], by the condensation of 3,3,3-trichloropropene with 1,1-dichloroethylene. It was found that a mixture of products is formed in this reaction. Fractionation through a column gave pure 1,1,5,5,5-pentachloro-1-pentene, b.p. 71° (1.5 mm); n_D^{20} 1.5108; d_4^{20} 1.4771; found MR 49.14; calculated for $C_5H_5Cl_5$ F MR 49.16 and 1,1,5,5-tetrachloro-1,4-pentadiene, b.p. 57° (1.5 mm); n_D^{20} 1.5197; d_4^{20} 1.4307; found MR 43.73; calculated for $C_5H_4Cl_4$ 2F, MR 43.82.

Found %: C 28.74; 28.78; H 1.90; 2.00. $C_5H_4Cl_4$. Calculated %: C 29.16; H 1.96.

The total yield of these two products was 60-70%, and the relative amounts depended on the condensation conditions, in particular the temperature and quality of aluminum chloride. Glutaric acid was prepared from 1,1,5,5-tetrachloro-1,4-pentadiene by hydrolysis with sulfuric acid.

Chlorine was passed at 20-25° through a mixture of 62 g of 1,1,5,5,5-pentachloro-1-pentene and 75 g of 93% sulfuric acid until hydrogen chloride ceased to be evolved. The mixture was diluted with water and extracted with chloroform. Acidic products were removed from the chloroform layer by washing with 10% sodium hydroxide solution. Acidification of the alkaline extract gave 2,5,5,5-tetrachlorovaleric acid, m.p. 82-83° (from benzene + petroleum ether).

Found %: C 24.80; 24.90; H 2.47; 2.49; Cl 59.43; 58.75 $C_5H_6Cl_4O_2$. Calculated %: C 25.02; H 2.52; Cl 59.12.

Yield 32 g (52%).

Action of Chlorine on 3,3,3-Trichloropropene in Sulfuric Acid. 3,3,3-Trichloropropene (21 g) and concentrated sulfuric acid (20 g) were mixed with cooling to about −30°. Chlorine was passed through the mixture at 0–10° until saturation was attained. After dilution with water, the organic layer was separated, washed with water, and dried with sodium sulfate. Distillation gave 14 g of 1,1,1,2,3-pentachloropropane, b.p. 54–56° (4 mm); n_D^{20} 1.5100 the literature [7] gives b.p. 64–65° (8 mm) and n_D^{20} 1,5105 and 11 g of bis-2,3,3,3-tetrachloropropyl sulfate, b.p. 189–190° (2 mm), m.p. 46–47° (from petroleum ether).

Found %: C 15,35; 15,58; H 1,26; 1,26; Cl 60,78; 61,06. $C_6Cl_8H_6SO_4$. Calculated %: C 15,73; Cl 61.30.

Hydrolysis of this sulfuric ester in acid medium gave 2,3,3,3-tetrachloro-1-propanol, m.p. 39–40°. In admixture with tetrachloropropanol obtained by the action of chlorine on 3,3-dichloro-2-propen-1-ol it melted at 39–40°.

Action of Chlorine on 3,3,3-Trichloropropene in Acetic Acid. Chlorine was passed at 50° through a solution of 28 g of 3,3,3-trichloropropene in 50 g of glacial acetic acid until no further reaction occurred. Acetic acid was distilled off, and the residue was vacuum-distilled. The products isolated were 23 g of 1,1,1,2,3-pentachloropropane, b.p. 65–66° (8 mm) and n_D^{20} 1,5102 and 9 g of 2,3,3,3-tetrachloropropyl acetate, b.p. 81–82° (2 mm); n_D^{20} 1.4858; d_4^{20} 1,4905; found MR 46.20; calculated for $C_5H_6Cl_4O_2$ MR 46.41.

Found %: C 24,78; 24,70; H 2,45; 2,45; Cl 59,77; 60,05. $C_5H_6Cl_4O_2$; Calculated %: C 25,02; H 2,52; Cl 59,12.

Treatment of this acetic ester with methanol in presence of hydrochloric acid gave 2,3,3,3-tetrachloro-1-propanol, identical with the tetrachloropropanol obtained by the action of chlorine on 3,3-dichloro-2-propen-1-ol.

Preparation of 3,3-Dichloro-2-propenyl Acetate. A mixture of 58 g of 3,3,3-trichloropropene, 40 g of calcined sodium acetate, and 75 ml of glacial acetic acid was boiled for 12 hours. The mixture was diluted with water, and the organic layer was separated, washed with water, and dried over calcium chloride. Distillation gave 43 g (71%) of 3,3-dichloro-2-propenyl acetate, b.p. 71–72° (14 mm); n_D^{20} 1,4650; d_4^{20} 1,2846; found MR 36,36; calculated for $C_5H_6O_2Cl_2$ F MR 36.21.

The literature [11] gives b.p. 116 − 117° (103 mm); n_D^{20} 1.4652.

Found %: Cl 41,34; 41,06. $C_5H_6O_2Cl_2$. Calculated %: Cl 41,95.

Preparation of 3,3-Dichloro-2-propen-1-ol. This was prepared by the action of methanol in presence of hydrochloric acid on 3,3-dichloro-2-propenyl acetate, prepared as described above. The alcohol had b.p. 56–57° (4 mm); n_D^{20} 1.4945; d_4^{20} 1.3763; found MR 26.88; calculated for $C_3H_4OCl_2$ F MR 26.85.

Found %: C 27,96; 28,04; H 3,25; 3,19. $C_3H_4OCl_2$. Calculated %: C 28,37; H 3,17.

Action of Chlorine on 3,3-Dichloro-2-propen-1-ol. Chlorine and hydrogen chloride were passed through a solution of 25 g of 3,3-dichloro-2-propen-1-ol in 25 ml of hydrochloric acid and 25 ml of ether saturated with hydrogen chloride at a temperature of −5° to 0° until no further reaction occurred (increase in weight 13 g). The mixture was diluted with water, and the organic layer was separated, washed with sodium carbonate solution and with water, and dried over sodium sulfate. Distillation gave 25 g (65%) of 2,3,3,3-tetrachloro-1-propanol, b.p. 78° (5 mm) and m.p. 39–40° (from petroleum ether) (the literature [12] gives m.p. 38–39°), and 5 g of a residue boiling up to 170° (5 mm).

Found %: C 19,60; 19,57; H 2,11; 2,01 $C_3H_4Cl_4O$. Calculated %: C 19,50; H 2,04.

When 3,3-dichloro-2-propen-1-ol was treated with chlorine in chloroform solution, reaction was accompanied by vigorous evolution of hydrogen chloride. Only 21% of the chlorine-addition product (2,3,3,3-tetrachloro-

propanol) was obtained, but a large amount of a mixture of high-boiling compounds was obtained.

Action of Chlorine on 1,1-Dichloro-3-methoxypropene. The reaction was carried out as described previously [1]. Fractionation of the products through an efficient column gave a pentachloro compound in 62% yield: b.p. 97-98° (5.5 mm); 81-82° (1.5 mm); n_D^{20} 1.5070; d_4^{20} 1.5713.

Boiling of 36 g of this pentachloro compound with 200 ml of methanol in presence of 1 ml of hydrochloric acid gave 26 g (90%) of 2,3,3,3-tetrachloro-1-propanol, m.p. 38-39° (from petroleum ether). A mixture of this with the tetrachloropropanol obtained by the action of chlorine on 3,3-dichloro-3-propen-1-ol melted at 38-39°.

The pentachloro compound therefore has the structure $CCl_3CHClCH_2OCH_2Cl$.

This pentachloro compound was obtained in 50% yield also by the action of paraform and hydrogen chloride in chloroform on 2,3,3,3-tetrachloro-1-propanol: b.p. 91-92° (2 mm); n_D^{20} 1.5065; d_4^{20} 1.5711; found MR 46.63; calculated for $C_4H_5Cl_5O$ MR 46.55.

Found %: C 19.60; 19.57; H 2.11; 2.01. $C_4H_5Cl_5O$. Calculated %: C 19.50; H 2.04.

SUMMARY

1. It was shown that compounds of the type $CCl_2 = CH(CH_2)nX$ react with chlorine in a neutral medium with formation of a mixture of saturated polychloro hydrocarbons and hydrogen chloride. When this reaction is carried out in presence of concentrated sulfuric acid at 0-15° without irradiation, smooth addition of chlorine at the double bond occurs.

2. It was found that reaction of compounds of structure $CCl_2 = CH(CH_2)n\,X = H, Cl, COOH, CCl_3$) with chlorine proceeds by "conjugated addition" only when the medium is a concentrated strong mineral acid (sulfuric or perchloric) with formation (after hydrolysis) of a α- chloro carboxylic acids. In phosphoric acid, and also in carboxylic acids, neutral chlorination products are obtained.

3. When chlorine reacts with 3,3,3-trichloropropene in glacial acetic or concentrated sulfuric acid, 2,3,3,3-tetrachloropropyl acetate or sulfate is obtained, respectively. This confirms that the trichloromethyl group shows the orienting effect characteristic of an electron-accepting group.

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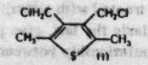
ACTION OF WATER ON 3,4-BISCHLOROMETHYL-2,5-DIMETHYLTHIOPHENE

Ya. L. Goldfarb and M. S. Kondakova

In the course of a study of the properties of 3,4-bischloromethyl-2,5-dimethylthiophene (I) it became necessary to study its behavior toward water at a moderate-temperature (70-80°).



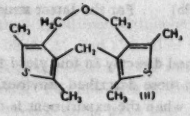
(I)

It might be supposed that, as an analog of 2-thenyl chloride, which is readily affected by nucelophilic reagents [1], the compound (I) would readily undergo hydrolysis, even under such mild conditions, with formation of a compound or compounds containing an intra- or inter-molecular oxygen bridge and also compounds containing an alcohol grouping. In this connection it must be mentioned that Steinkopf [2] heated 3,4,5-tribromo-2-thenyl bromide with water in presence of sodium carbonate and obtained the corresponding bromine-substituted dithenyl ether. Another relevant observation is that of Cairns and McKusick on the formation of ethyl 2-thenyl ether by reaction of 2-thenyl chloride with aqueous alcohol.

Our first experiments already showed that the bischloromethyl compound (I) does indeed undergo change in even a very short treatment with hot water. Outwardly this is clear from the fact that, after it has melted, the compound (I) slowly begins to solidify. By repeated recrystallization of the mass so obtained we succeeded in isolating crystals of m.p. 154-155° in a yield that varied from one experiment to another. Further study of this substance showed that, as had been supposed, it contained ether oxygen, but it corresponded in composition to the formula $C_{18}H_{18}OS_2$, with an odd number of carbon atoms. This result can be explained only by the view that the formation of a compound $C_{18}H_{18}OS_2$ in the course of the reaction of (I) with water is associated with the elimination of one carbon atom in the form of formaldehyde. Formaldehyde is indeed found in the filtrate obtained in separation of the product of the reaction of (I) with water.

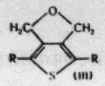
It is pertinent to mention here that this kind of scission of a C—C bond under conditions close to those described in this paper has been observed previously, for example in the hydrolysis of bromomethyl and hydroxymethyl derivatives of pyrrole, by Fischer and coworkers [3] and later by Corwin and coworkers [4]; as a result of this reaction, the corresponding methylenedipyrroles are obtained with elimination of formaldehyde. However, our case of carbon—carbon scission differs from those cited in that it occurs at a β-carbon not directly attached to the hetero atom of the ring.

Consideration of the data obtained on the composition and properties of the substance of m.p. 154-155° together with the nature of the original compound (I) enables us to assign the structure (II) to this compound.



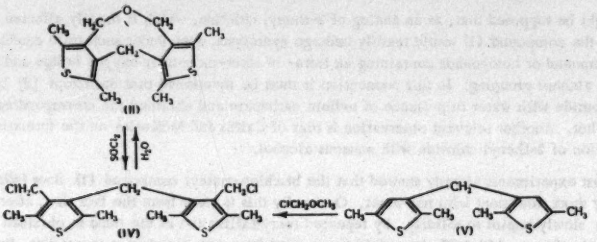
(II)

This formula indicates that the compound contains a condensed ring system built up from an eight-membered oxygen-containing ring and two thiophene rings, i.e. 1,3,7,9-tetramethyl-4H,6H,10H-dithieno [3,4-c,3', 4'-f] oxocin. The readiness with which the substance of m.p. 154-155° is formed may give rise to doubt about the correctness of this view of its structure, particularly since there is the possibility of the intramolecular ring-closure of (I) with formation of (III), which contains a hydrogenated furan ring:



(III)

However, further experiments, designed for the verification of the view that we have advanced, confirmed the correctness of the formula (II). Thus, when the compound (II) was submitted to the reaction described by one of us and Smorgonsky [5] - which consists in the splitting of ethers with thionyl chloride in presence of stannic chloride - it was converted into a dichloro compound, which was found to be identical with 3,3'-methylenebis [4-(chloromethyl)-2,5-dimethylthiophene] (IV), which we have prepared by the chloromethylation of 3,3'-methylenebis[2,5-dimethylthiophene] (V) [6]. When treated with water, the bischloromethyl compound (IV) again gives the cyclic ether (II). These reactions, particularly the last, give poor yields, for other, parallel reactions occur. However, they make it possible to establish a relationship between the various compounds.



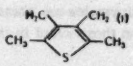
(II)

(IV)

(V)

The structure (II) for the compound of m.p. 154-155° is supported also by its dipole moment. This property was measured in E. N. Guryanova's laboratory at the L. Ya. Karpov Institute. The authors take this opportunity to express their thanks to E.N. Guryanova for her readiness to undertake this work and for carrying it out.

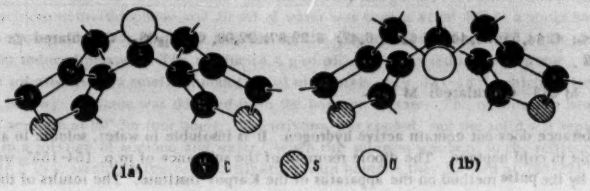
The value found for the dipole moment (1.42 D) is identical with the value calculated on the assumptions that the molecule is built up of two flat systems attached through the common carbon atom (I)



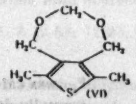
(I)

and that the oxygen completing the eight-membered ring is in the syn-position, as shown diagrammatically in (Ia) and not in the anti-position (Ib) For the latter structure (Ib), the calculated dipole moment is 2.4-2.5 D.

The compound (II) can be obtained directly in low yield from 2,5-dimethylthiophene by chloromethylation under conditions somewhat different from those described previously [6], namely, by replacement of concentrated hydrochloric acid by dilute (1:1) acid. When the experiment is carried out under such conditions, apart from the compound (II), a small amount of another compound of composition $C_9H_{12}O_2S$, m.p. 75-75.5°, can be isolated.

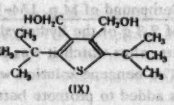


This compound does not contain active hydrogen and appears to be the product (VI) of the condensation of 3,4-bischloromethyl-2,5-dimethylthiophene:



However, this view on the structure of the compound (VI) is in need of experimental confirmation.

In view of these results, it was of interest to study the behavior of other 2,5-dialkyl-3,4-bischloromethylthiophenes toward water. The investigation that we have undertaken in this direction, in which the behaviors of 2,5-di-tert-butyl-3,4-bischloromethylthiophene (VII) and 3,4-bischloromethyl-2,5-diethylthiophene (VIII) were examined, cannot be regarded as complete, mainly because we succeeded in isolating the reaction products in only insignificant amounts. With water, the first of these two chloromethyl derivatives forms a cyclic ether, probably of structure (III) (R = $C(CH_3)_3$), m.p. 220°; with thionyl chloride (see above) this gives the original 2,5-di-tert-butyl-3,4-bischloromethylthiophene, which indicates that the structure (III) is correct for the compound of m.p. 220°. Together with this ether, 2,5-di-tert-butyl-3-4-thiophenedimethanol (IX) is formed:



This was found to be identical with the product of the hydrolysis of the corresponding diacetic ester obtained by action of sodium acetate on (VII). From the product obtained by reaction of 3,4-bischloromethyl-2,5-diethylthiophene with water we succeeded in isolating only an insignificant amount of compound of m.p. 119°, which corresponded in composition to formula (III) (R=C_2H_5). We could not detect the presence of condensed systems of the type (II) among the products of the reaction of (VII) and (VIII) with water.

At present it does not appear to be possible to give a satisfactory explanation of the surprising difference in behavior between the analogous systems (I), (VII), and (VIII) in reaction with water. However, we hope to return to this question later.

EXPERIMENTAL

1. Action of Water on 3,4-Bischloromethyl-2,5-dimethylthiophene. A stirred mixture of 6 g of 3,4-bischloromethyl-2,5-dimethylthiophene, m.p. 68-68.5°, and 120 ml of water was heated at 70-80° in a water bath for 1 hour 15 minutes. After one hour at room temperature, the solid reaction product was filtered off, ground, and washed with small amounts of acetone. The colorless product (2 g) melted at 153-155° (it showed a preliminary fusion effect). Recrystallization from acetone gave long colorless needles, m.p. 154-155.5°.

Further recrystallization from acetone and heptane did not affect the melting point.

Found %: C 64.55; 64.44; H 6.41; 6.47; S 22.87; 22.98. $C_{15}H_{18}OS_3$. Calculated %: C 64.74; H 6.47 S 23.02.

Found: M 263 Calculated: M 278.

The substance does not contain active hydrogen. It is insoluble in water, soluble in alcohol and benzene, difficulty soluble in cold heptane. The dipole moment of the substance of m.p. 154-155° was measured in benzene solution at 25° by the pulse method on the apparatus of the Karpov Institute. The results of the measurements are given in the table.

TABLE

c	E	d
0	2.2714	0.87269
0.023	2.2726	0.87293
0.051	2.2738	0.87322
0.093	2.2753	0.87369
0.117	2.2762	0.87387
0.149	2.2774	0.87428

P_{∞} = 124.1

μ = 1.42

Note: c — mole percentage of solution; E — dielectric constant of solution; d — density of solution; P_{∞} — polarization of substance at infinite dilution.

Extrapolation to infinite dilution was carried out by the Hedestrand method. The dipole moment was calculated from the formula:

$$\mu = 0.22 \sqrt{P_{\infty} - P_E}.$$

P_E was calculated additively on the basis of the experimentally determined refraction of tetramethylthiophene.

Formaldehyde was detected in the aqueous filtrate with the aid of the reaction of Rimini et al. [7]. The formaldehyde was isolated as its 2,4-dinitrophenylhydrazone, which melted at 163.5° after recrystallization from alcohol. In admixture with a known sample of formaldehyde 2,4-dinitrophenylhydrazone, it melted without depression.

Found % N 26.54. $C_7H_6N_4O_4$. Calculated % N 26.66.

2. Action of Thionyl Chloride on the Compound of M.p. 154-155°. Thionyl chloride (0.3 g) and stannic chloride (two drops) were added to a solution of 2.3 g of the hydrolysis product in 30 ml of dry benzene, and the mixture was heated in a water bath for five hours, after which it was left at room temperature overnight. The reaction product was decomposed with water. The benzene solution was separated and washed with water and with 5% sodium bicarbonate solution (ether was added to promote better separation of the layers). Benzene was distilled off under reduced pressure, and the solid residue (1.9 g) was washed with heptane and then crystallized twice from hot heptane.

The crystals so obtained melted at 171-172°. In a mixture test with the substance obtained by the chloromethylation of 3,3'-methylenebis [2,5-dimethylthiophene] there was no depression.

Found % C 54.32; 54.34; H 5.73; 5.15. $C_{15}H_{18}Cl_2S_3$. Calculated % C 54.05; H 5.40.

3. Action of Water on 3,3'-Methylenebis [4-(chloromethyl)-2,5-dimethylthiophene]. A stirred mixture of 2.6 g of 3,3'-methylenebis[4-(chloromethyl)-2,5-dimethylthiophene] and 120 ml of water was heated at 60-80° in a water bath for four hours. The mixture was cooled, and the solid product was filtered off and dissolved in hot heptane. After several days in a refrigerator, the heptane solution gave 0.9 g of crystals, m.p. 138-148°. After recrystallization from acetone the melting point range was unchanged. The substance was again heated with water at 90-95° for eight hours, after which the product was filtered off and crystallized from acetone; m.p. 155°, undepressed by admixture of the substance obtained by the action of water on 3,4-bischloromethyl-2,5-dimethylthiophene.

Found % C 65.01; 65.21; H 6.48; 6.44; S 22.60; 22.50. $C_{15}H_{18}OS_3$. Calculated % C 64.71; H 6.47; S 23.02.

4. Action of Water on 2,5-Di-tert-butyl-3,4-bischloromethylthiophene. A stirred mixture of 5 g of 2,5-di-tert-butyl-3,4-bischloromethylthiophene and 70 ml of water was heated at 80-90° in a water bath for six hours. The solid reaction product was dissolved in benzene, the solution was washed with water, and benzene was distilled off under reduced pressure. The residue (4.4 g of oil) was dissolved in hot heptane. After standing in a refrigerator, the solution yield a small amount (0.2 g) of crystals, m.p. 141-143°, which melted at 162.5° after compound, see below). Heptane was distilled from the heptane filtrate. The residue was heated with 80 ml of water and a little acetone at 90° for four hours. The mixture was cooled, and the solid was separated from the water and dissolved in a mixture of acetone and water. When this solution was kept in the refrigerator for several days, some crystals (0.5 g) separated after recrystallization from heptane they melted at 220-221°.

Found %: C 70.41; 70.35; H 9.23; 9.39; S 13.12; 13.20. $C_{14}H_{22}OS$. Calculated %: C 70.58; H 9.24; S 13.44.

Water was added to the acetone-water filtrate, and the mixture was again stirred in the water bath (90°) for 6 hours 30 minutes. The resulting semisolid mass was dissolved in hot heptane. On cooling, 0.4 g of crystals, m.p. 167-169°, separated. After recrystallization from heptane they melted at 166-167°.

Found %: C 65.29; 65.34; H 9.22; 9.15; S 12.68; 12.95. $C_{14}H_{24}O_2S$. Calculated %: C 65.62; H 9.37; S 12.50.

The substance was found to be identical with the dihydroxy compound obtained by the hydrolysis of the diacetic ester of 2,5-di-tert-butyl-3,4-thiophenedimethanol.

5. Diacetic Ester of 2,5-Di-tert-butyl-3,4-thiophenedimethanol. Anhydrous sodium acetate (1.8 g) was added to a solution of 3 g of 2,5-di-tert-butyl-3,4-bischloromethylthiophene in 10 ml of glacial acetic acid. The mixture was heated at 60-70° in a water bath for 4 hours 30 minutes. The mixture was cooled, and the precipitate was filtered off. On standing, the filtrate yielded 1.2 g of crystals, m.p. 134-135°. Evaporation of the filtrate gave a further 1.2 g of m.p. 135° (preliminary fusion occurred at a lower temperature). After recrystallization from heptane it melted at 135-135.5°.

Found %: C 63.50; 63.50; H 8.25; 8.04; S 9.43; 9.60. $C_{18}H_{28}O_4S$. Calculated %: C 63.52; H 8.22; S 9.41.

6. Hydrolysis of the Diacetic Ester of 2,5-Di-tert-butyl-3,4-thiophenedimethanol. The diacetic ester of 2,5-di-tert-butyl-3,4-thiophenedimethanol (2.3 g) was added to an alcoholic solution of sodium ethoxide prepared from 0.04 g of sodium and 10 ml of absolute ethanol. The mixture was stirred at room temperature for seven hours and then set aside for two days. The precipitate that formed was filtered off and washed with alcohol. Alcohol was distilled from the filtrate, and the residue (1.4 g) was crystallized from heptane. The product, amounting to 0.5 g, melted at 166-167°. Recrystallization from heptane did not affect the melting point.

Found %: C 66.05; 66.13; H 9.42; 9.29; S 12.14; 11.96. $C_{14}C_{24}O_2S$. Calculated %: C65.62; H 9.37; S 12.50.

7. Action of Thionyl Chloride on the Substance of M.p. 219-220° obtained by the Action of Water on 2,5-Di-tert-butyl-3,4-bischloromethylthiophene. A mixture of 0.6 g of the substance of m.p. 219-220°, 10 ml of dry benzene, 0.3 g of thionyl chloride, and one drop of stannic chloride was heated in a water bath for three hours. The mixture was cooled and poured into water, and the benzene layer was separated and washed with 5% sodium carbonate solution and with water. The residue remaining after removal of benzene was dissolved in acetic acid. The crystals that separated when the solution was kept in a refrigerator were filtered off and washed with heptane and alcohol. After recrystallization from acetic acid they melted at 85.5-86.5°. In admixture with 2,5-di-tert-butyl-3,4-bischloromethylthiophene [6] they melted at the same temperature.

8. Action of Water on 3,4-Bischloromethyl-2,5-diethylthiophene. A stirred mixture of 6 g of 3,4-bischloromethyl-2,5-diethylthiophene and 140 ml of water was heated at 90-95° in a water bath for 1 hour 20 minutes. The substance was gradually converted into reddish oil. The aqueous layer was poured off, and the oil was dissolved in hot acetone. The crystals that separated when the solution was kept in a refrigerator (0.3 g) melted at 119°, and the melting point was not affected by recrystallization from heptane.

Found %: C 66.08; 66.33; H 7.70; 7.94; S 17.21; 17.45. $C_{10}H_{14}OS$. Calculated %: C 66.00; H 7.70; S 17.60.

9. Action of Formaldehyde on 2,5-Dimethylthiophene in presence of Dilute Hydrochloric Acid. A mixture of 5.6 g of 2,5-dimethylthiophene, 10 ml of concentrated hydrochloric acid (d = 1.18), 10 ml of water, and 10 ml of 37% formaldehyde was heated at 75° in a water bath for one hour. The mixture first became blue, then green, and finally brown. The mixture was kept at room temperature for several hours, and the precipitate that formed was then separated, washed with water, and dissolved in benzene. The benzene solution was washed with water and with sodium carbonate solution. Benzene was distilled off, and vacuum distillation of the residue gave the fractions:

Fraction I, b.p. 130-150° (7 – 8 mm); 1.5 g
Fraction II, b.p. 150-210° (7 – 8 mm); 2.6 g

The resinous residue in the flask (1.6 g) was not investigated. Fraction I was dissolved in hot heptane, and the solution was placed in a refrigerator. Crystals separated (0.6 g, m.p. 71-72°); they did not contain halogen. After two recrystallizations from heptane they melted at 75-75.5°.

Found %: C 58.67; 58.58; H 6.30; 6.15; S 17.43; 17.51. $C_9H_{12}O_2S$. Calculated %: C 58.69; H 6.52; S 17.40.

The substance did not contain active hydrogen; it sublimed when left in the open at room temperature.

Found: M 181; 179 Calculated: M 184

Fraction II was dissolved in hot heptane. When the heptane solution was cooled, 0.9 g of crystals separated (m.p. 92-120°). After repeated crystallization from heptane the substance melted at 154-155°. In admixture with the substance obtained by the action of water on 3,4-bischloromethyl-2,5-dimethylthiophene there was no depression of melting point.

SUMMARY

1. When 3,4-bischloromethyl-2,5-dimethylthiophene was treated with water, the condensed system 1,3,7,9-tetramethyl-4H, 6H, 10H-dithieno[3,4-c,3',4'-f]oxocin (II) was formed.

2. The structure of this product was confirmed by its synthesis from 3,3'-methylenebis[2,5]dimethylthiophene] by the results of the splitting of the product with thionyl chloride, and by the results of dipole moment measurements.

3. No analogs of the compound (II) could be detected among the hydrolysis products of 2,5-di-tert-butyl-3,4-bischloromethylthiophene and of 3,4-bischloromethyl-2,5-diethylthiophene.

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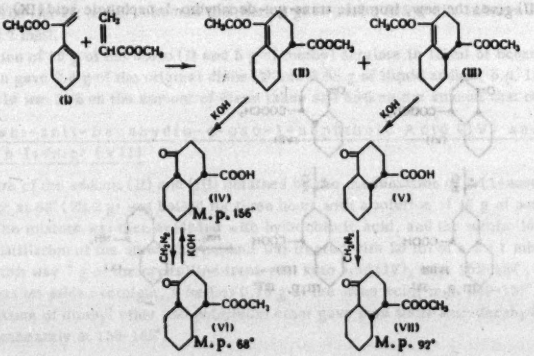
* T. p. = C. B. Translation pagination.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 14. CONDENSATION OF 1-(1-ACETOXYVINYL)CYCLOHEXENE WITH METHYL ACRYLATE

I. N. Nazarov, V. F. Kucherov, and G. M. Segal

As we have pointed out previously [1], in the condensation of various dienophiles with 1-(1-acetoxyvinyl) cyclohexene[1-(1-cyclohexen-1-yl)ethenol acetic ester] (I), good yields are obtained of adducts which are readily converted by hydrolysis into polycyclic compounds containing an α-keto group in the nucleus. It is characteristic of the diene (I) that in reaction with methyl acrylate it forms a mixture of the stereoisomeric adducts (II) and (III), which are epimeric with respect to the hydrogen at C-8a and which are hydrolyzed to the isomeric decahydro-4-oxo-1-naphthoic acids (IV) and (V), with trans configuration of the rings. This fact prompted us to make a detailed study of the effect of temperature on steric directivity in a diene reaction of this sort with the object of making a further investigation of the stereochemistry of the isomeric decahydro-1-naphthoic acids. It was found that in the condensation of the diene (I) with methyl acrylate the ratio in which the isomeric adducts (II) and (III) are formed depends on temperature, but the character of the dependence is quite different from that found in the case of 1-vinylcyclohexene [2].



In order to isolate the individual isomers we hydrolyzed the liquid mixture of the adducts (II) and (III) with 20% potassium hydroxide solution, and crystallization then gave trans-anti-decahydro-4-oxo-1-naphthoic acid (IV), m.p. 156°; from the liquid residue, after esterification with diazomethane, the isomeric trans-syn keto acid (V) was readily isolated in the form of its ester (VII), m.p. 92°. Treatment of the trans-anti acid (IV) with diazomethane gave the corresponding ester (VI), m.p. 68°, which could be quantitatively hydrolyzed to the original acid. However, attempts to obtain the pure trans-syn keto acid (V) by hydrolysis of its ester (VII) were not successful, since partial isomerization occurred with formation of a mixture of acids that was difficult to separate.

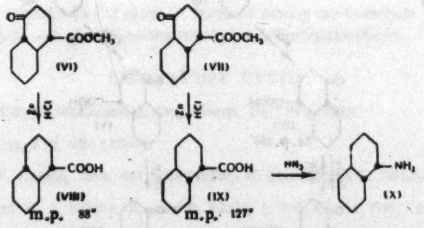
By the use of this method, which is described in detail in the experimental part, we succeeded in showing that, in spite of the possibility of partial isomerization of the syn adduct (III) in the course of hydrolysis, the amount formed of the anti isomer (II) diminishes with rise in the temperature of the condensation. The relative amounts of the isomers can be seen from the table.

TABLE

Condensation temperature (°C)	Duration of condensation	Total yield of adduct (%)	Amount of isomers Keto acid (IV)	Keto ester (VII)
20	65 days	24	62	6
80	20 hrs	57	46	22
100	15 hrs	80	43	23
180	6 hrs	65	37	24

The results show that, in contrast to the behavior of 1-vinylcyclohexene, condensation of 1-(1-acetoxyvinyl)cyclohexene with methyl methacrylate yields mainly the anti isomer (II), readily isolated in the form of the trans-anti keto acid (IV). However, the amount of this diminishes appreciably with rise of temperature, whereas the yield of the syn isomer (III), isolated in the form of the trans-syn keto ester (VII), increases very greatly, attaining 24% at 180°. The trans-anti keto ester (VI) is very stable thermally, and after being heated at 250° for two hours it can be recovered unchanged almost quantitatively. On the other hand, the trans-syn isomer (VII) is isomerized considerably under these conditions, being converted to an extent of more than 50% into an inseparable mixture of isomeric keto esters.

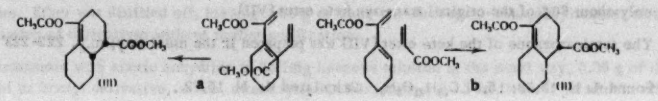
The spatial structures of the isomeric adducts were readily proved by Clemmensen reduction of the keto esters (VI) and (VII). It was found that the trans-anti keto ester (VI) gives a good yield of the previously prepared [2] trans-anti-decahydro-1-naphthoic acid (VIII), m.p. 88°, m.p. of amide 223° [3]. Similar reduction of the trans-syn keto ester (VII) gives the new, isomeric trans-syn-decahydro-1-naphthoic acid (IX), m.p. 126-127°, m.p. of amide 192-193°.



In order to confirm the configuration of the trans-syn acid (IX) it was converted by the Schmidt reaction into the known trans-syn-decahydro-1-naphthylamine (X), from which the acetyl derivative, m.p. 128-130°, and benzoyl derivative, m.p. 110-111°, were prepared; their properties coincided with those reported in the literature. These results show that alkaline hydrolysis of the acetylated enol group in the epimeric adducts (II) and (III) leads exclusively to compounds of the tran-decahydronaphthalene series, so that the use of 1-(1-acetoxyvinyl)cyclohexene (I) in various diene condensations is of particular interest.

The fact that the main product of the diene reaction of 1-(1-acetoxyvinyl) cyclohexene with methyl acrylate is the anti isomer (II) can be explained by the steric and electrostatic effects of the electronegative acetylated enol group present in the molecule of the diene (I). As a result of these effects the mutual spatial orientation of the components according to scheme (a) is rendered difficult, whereas favorable conditions are created

for orientation in accordance with scheme (b) (contrary to the rule of "accumulation of unsaturation") with formation of the anti isomer (II).



With rise in the condensation temperature there is a rise also in the probability of the molecules' coming together according to scheme (a) with formation of the syn isomer (III).

EXPERIMENTAL

Condensation of 1-(1-Acetoxyvinyl)cyclohexene with Methyl Acrylate

a) A solution of 28 g of 1-(1-acetoxyvinyl) cyclohexene (I) [1] and 13.8 g of methyl acrylate in 60 ml of dry benzene was boiled in presence of a little pyrogallol for 20 hours. Solvent was distilled off, and vacuum distillation of the residue gave 12.5 g of the original diene (I) and 23.2 g (57.4%) of a liquid mixture of adducts (II) and (III), b.p. 130-132.5° (2 mm) and n_D^{20} 1.4910.

Found %: C 66.34; 66.33; H 8.00; 8.04. $C_{14}H_{20}O_4$. Calculated %: C 66.24; H 7.99.

b) Similarly, a solution of 8 g of the diene (I) and 4 g of methyl acrylate in 15 ml of dry toluene was boiled for 15 hours. Vacuum distillation of the product gave 9.4 g (80%) of a mixture of adducts (II) and (III), b.p. 133-135° (2 mm); n_D^{20} 1.4910; d_4^{20} 1.1050.

c) A mixture of 10 g of the diene (I), 5 g of methyl acrylate, and 15 ml of dry benzene was heated in a steel tube at 175-180° for six hours. Vacuum distillation gave 10.3 g (65%) of a mixture of adducts (II) and (III), b.p. 133-135° (2 mm).

d) A solution of 10 g of the diene (I) and 5 g of methyl acrylate in 15 ml of benzene was left at 20° for 65 days. Distillation gave 6.4 g of the original diene (I) and 3.65 g of liquid adduct, b.p. 135-137° (3 mm) and n_D^{20} 1.4920. The yield was 24% on the amount of diene taken and 69% on the amount that reacted.

Isolation of trans-anti-Decahydro-4-oxo-1-naphthoic Acid (IV) and the Methyl Ester of the trans-syn Isomer (VII)

The mixture of the adducts (II) and (III) obtained by the condensation of 1-(1-acetoxyvinyl) cyclohexene with methyl acrylate at 80° (23.2 g) was boiled for three hours with a solution of 46 g of potassium hydroxide in 200 ml of water. The mixture was then acidified with hydrochloric acid, and the semisolid product was extracted with ether. After distillation of the ether, the product was treated with 25 ml of a 2 : 1 mixture of ether, and petroleum ether, and in this way 7 g of the crystalline trans-anti keto acid (IV), m.p. 152-154°, was obtained. When the mother liquor was set aside overnight, a further 0.15 g of the same acid, m.p. 149-151°, separated. Crystallization from a mixture of diethyl ether and petroleum ether gave pure trans-anti-decahydro-4-oxo-1-naphthoic acid (IV), melting constantly at 155-156°.

Found %: C 67.42; 67.59; H 8.20; 8.18. $C_{11}H_{16}O_3$. Calculated %: C 67.32; H 8.21.

The amide was prepared; m.p. 201-202° after two recrystallizations from alcohol.

The residue after the separation of the trans-anti acid (IV) was treated with ethereal diazomethane, ether was distilled off, and the liquid product was dissolved in 15 ml of petroleum ether. Standing overnight gave 2.65 g of methyl trans-syn-decahydro-4-oxo-1-naphthoate (VII), m.p. 87-89°. A further 0.65 g of the same ester, m.p. 85-87°, was obtained by partial evaporation of solvent. Crystallization from petroleum ether gave pure trans-syn ester (VII), m.p. 91-92°.

Found %: C 68.72; 68.77; H 8.85; 8.71. $C_{12}H_{18}O_3$. Calculated %: C 68.54; H 8.63.

An attempt to hydrolyze the ester (VII) by boiling it with a 20% solution of potassium hydroxide resulted in the formation of a mixture of isomeric acids, from which, by treatment with diazomethane, we succeeded in isolating only about 60% of the original trans-syn keto ester (VII).

The semicarbazone of the keto ester (VII) was prepared in the usual way; m.p. 222-223° (from methanol).

Found %: N 15.58; 15.57. $C_{13}H_{21}O_3N_3$. Calculated %: N 15.72.

With the object of obtaining further amounts of the crystalline isomers, the residue after the isolation of the ester (VII) was again hydrolyzed with 20% sodium hydroxide solution, and the procedure described above was repeated. As a result, a further 1.1 g of the trans-anti keto acid (IV) and a further 1.15 g of the trans-syn keto ester (VII) were obtained.

By a similar method the isomers were isolated also from the mixtures of adducts (II) and (III) formed at other temperatures. Thus, from 3.65 g of adduct prepared at 20°, 1.75 g of the trans-anti keto acid (IV) and 0.18 g of the trans-syn keto ester (VII) were isolated, whereas from 8 g of adduct prepared at 180° the amounts of these isomers were 2.35 g and 1.6 g, respectively.

Methyl trans-anti-Decahydro-4-oxo-1-naphthoate (VI)

A solution of 2 g of the trans-anti keto acid (IV) in ether was treated with excess of ethereal diazomethane. Removal of solvent gave 1.9 g of the trans-anti keto ester (VI), m.p. 66-68°. Crystallization from petroleum ether did not affect the melting point (67-68°).

Found %: C 68.73; 68.74; H 8.69; 8.53. $C_{12}H_{18}O_3$. Calculated %: C 68.54; H 8.63.

Hydrolysis of this ester with boiling 20% potassium hydroxide solution gave the original trans-anti keto acid (IV). The semicarbazone prepared in the usual way from the trans-anti keto ester (VI) melted at 225-226° after crystallization from methanol; the melting point was depressed by admixture of the semicarbazone of the trans-syn keto ester (VII) (205-211°).

Found %: N 15.96; 16.08 $C_{13}H_{21}O_3$. Calculated %: N 15.72.

trans-anti-Decahydro-1-naphthoic Acid (VIII)

A mixture of 0.35 g of the trans-anti keto ester (VI), 2 g of amalgamated zinc, and 5 ml of concentrated hydrochloric acid was boiled for five hours. The crystalline product obtained on cooling was filtered off: 0.25 g of the trans-anti acid (VIII), m.p. 85-87°, raised to 87-88° by crystallization from petroleum ether; a mixture test with a known sample [2] showed no depression. The amide of the acid had m.p. 222-223°, undepressed by admixture of a known sample [3].

trans-syn-Decahydro-1-naphthoic Acid (IX)

Analogous reduction of 3 g of the trans-syn keto ester (VII) gave 1.5 g of the trans-syn acid (IX), which, after two crystallizations from a mixture of diethyl ether and petroleum ether had a constant melting point of 126-127°, which was depressed by admixture of the previously described [2] cis-syn-decahydro-1-naphthoic acid (98-105°).

Found %: C 72.12; 72.29; H 9.74; 9.79 $C_{11}H_{18}O_2$. Calculated %: C 72.49; H 9.95

The amide was prepared; after crystallization from alcohol it melted at 192-193°.

Found %: C 72.67; 72.88; H 10.45; 10.63 $C_{11}H_{19}ON$. Calculated %: C 72.76; H 10.56.

trans-syn-Decahydro-1-naphthylamine (X) and its Derivatives

Concentrated sulfuric acid (11 ml) was added to a solution of 1 g of trans-syn-decahydro-1-naphthoic

acid (IX) in 28 ml of dry chloroform. The mixture was heated to 40°, and with constant stirring 0.8 g of sodium azide was gradually added in small portions. The mixture was heated at 50° for one hour and then poured into 30 ml of cold water. The aqueous layer was separated, subjected to extraction with ether, and saturated with solid sodium hydroxide. The amine that separated was extracted with ether, and the extract was dried with potassium carbonate. Ether was distilled off, leaving 0.65 g of trans-syn-decahydro-1-naphthylamine, which was used for the preparation of derivatives without further purification.

By treatment with acetic anhydride in boiling benzene solution in the usual way, 0.35 g of the amine gave 0.35 g of its acetyl derivative, which, after crystallization from a 2 : 1 mixture of petroleum ether and diethyl ether, had m.p. 129-130°, which coincides with that reported in the literature [4].

Found %: N 7.10; 7.23 $C_{12}H_{21}ON$. Calculated %: N 7.17.

Benzoylation of 0.3 g of the amine in the usual way gave 0.3 g of its benzoyl derivative, which, after crystallization from petroleum ether had m.p. 110-111°, which coincides with that reported in the literature [4].

Found %: N 5.61; 5.65. $C_{17}H_{23}ON$. Calculated %: N 5.44.

Thermal Transformation of the Isomeric Decahydro-4-oxo-1-naphthoic Acids (VI) and (VII)

a) The trans-anti keto ester (VI) (1 g) was heated for two hours at 250°. Vacuum distillation of the product gave 0.9 g of a liquid, which immediately solidified and had m.p. 66-68°, undepressed by admixture of some of the original keto ester (VI).

b) The trans-syn keto ester (VII) (0.6 g) was heated for two hours at 240-250°. Crystallization of the dark-colored product from petroleum ether gave 0.25 g of the original keto ester (VII), m.p. 90-92°, and 0.3 g of a mixture of keto esters which could not be separated by crystallization.

SUMMARY

1. A study was made of the condensation of 1-(1-acetoxyvinyl)cyclohexene (I) with methyl acrylate, and it was shown that the ratio in which the epimeric adducts (II) and (III) are formed is dependent on the condensation temperature. It was shown that, in contrast to the case of the condensation of 1-vinylcyclohexene, the main product is the anti isomer (II), the amount of which diminishes with rise in temperature, there being a simultaneous increase in the yield of the isomeric syn adduct (III).

2. By alkaline hydrolysis of the mixture of adducts (II) and (III), the isomeric decahydro-4-oxo-1-naphthoic acids were isolated in the form of the trans-anti acid (IV) and the trans-syn ester (VII). The spatial configuration of these products were proved by Clemmensen reduction into the known isomeric acids of the trans-decahydronaphthalene series (VIII) and (IX).

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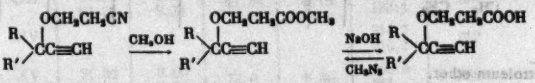
ACETYLENE DERIVATIVES

COMMUNICATION 176. SYNTHESIS OF 2-CARBOXYETHYL ETHERS OF ACETYLENIC ALCOHOLS AND OF THEIR ACID CHLORIDES AND AMIDES

I. N. Nazarov and G. A. Shvekhgeimer

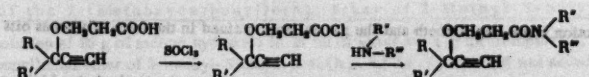
The hydrolysis of 2-cyanoethyl ethers of saturated alcohols and glycols to the corresponding 2-carboxyethyl ethers can be effected smoothly by heating them with concentrated hydrochloric acid [1]. On the other hand, when attempts are made to effect the acid hydrolysis of 2-cyanoethyl ethers of acetylenic alcohols under various conditions (treatment with concentrated hydrochloric acid at temperatures ranging from 20° to 100°, both without solvent, and also in presence of ether or glacial acetic acid), complete resinification occurs. Alkaline hydrolysis of 2-cyanoethyl ethers of acetylenic alcohols in aqueous or methanolic solution gives the expected acids, but in low yield. When alkaline hydrolysis is carried out in 50% aqueous methanol, transcyanoethylation occurs and 3-methoxypropionic acid is formed. As a convenient method is available for the conversion of 2-cyanoethyl ethers of acetylenic alcohols into the corresponding 2-(methoxycarbonyl)ethyl ethers [2], we decided to hydrolyze the latter with the object of preparing the 2-carboxyethyl ethers that we required. It was found that 2-(methoxycarbonyl)ethyl ethers of acetylenic alcohols are smoothly hydrolyzed at room temperature by methanolic sodium hydroxide with formation of the corresponding 2-carboxyethyl ethers in high yield:



The 2-carboxyethyl ethers of acetylenic alcohols prepared in this way are listed in Table 1. Results of analysis and molecular-weight determination (by titration) are given in Table 2.

When treated with diazomethane, the 2-carboxyethyl ethers of acetylenic alcohols are reconverted almost quantitatively into the original 2-(methoxycarbonyl)ethyl ethers.

When treated with thionyl chloride at 60°, the 2-carboxyethyl ethers are converted into the corresponding acid chlorides in more than 90% yield, and treatment of the products with ammonia or amines in ethereal solution gives the corresponding amides in almost theoretical yield:



When the 2-carboxyethyl ethers of acetylenic alcohols were treated with thionyl chloride in presence of pyridine by the method described previously [3], the main products were the acid anhydrides:

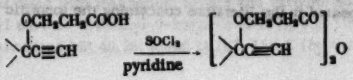
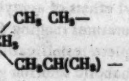
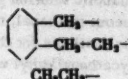
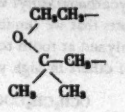


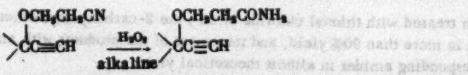
TABLE 1

Compound	R	R'	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated
I	C_2H_5	H	84	117—118(3.5)	1.4451	1.0292	40.35	40.26
II	n-C_3H_7	H	84	134—136(6)	1.4460	1.0076	44.99	44.87
III	i-C_3H_7	H	86	129—130(6)	1.4453	1.0065	44.91	44.87
IV	CH_3	CH_3	90	108—110(3.5)	1.4419	1.0263	40.21	40.26
V	C_2H_5	CH_3	87	118—120(4)	1.4470	1.0144	44.91	44.87
VI	n-C_3H_7	CH_3	94	128—130(4.5)	1.4460	0.9939	49.37	49.49
VII	n-C_5H_{11}	CH_3	90	155—157(4)	1.4517	0.9572	63.66	63.35
VIII	n-C_9H_{17}	CH_3	84	185—187(5)	1.4523	0.9376	73.12	72.59
IX	C_2H_5	C_2H_5	93	131—133(5)	1.4487	1.0006	49.29	49.49
X	n-C_3H_7	n-C_3H_7	81	144—146(4.5)	1.4503	0.9752	58.45	58.73
XI	i-C_3H_7	i-C_3H_7	79	144—146(5)	1.4505	0.9944	57.79	58.73
XII	$(CH_2)_4$		83	142—144(5)	1.4725	1.0751	47.44	47.29
XIII	$(CH_2)_5$		92	155—156(4.5) т. пл. 46—47°°	1.4775	1.0678	51.92	51.91
XIV			76	153—155(4)	1.4660	1.0460	55.65	56.53
XV			85	194— 95(5)	1.5005	—	—	—
XVI			82	174—176(4.5) т.пл.72—73.5°°	—	—	—	—

• From petroleum ether.

•• From cyclohexane.

Hydrolysis of the 2-cyanoethyl ethers of acetylenic alcohols with alkaline hydrogen peroxide [4] provided another method of preparing the corresponding amides:



However, this reaction is not very smooth and the amides are obtained in the form of viscous oils that are difficult to purify.

The acid chlorides and amides of 2-carboxyethyl ethers of acetylenic alcohols which we prepared are listed in Tables 3-5 (the numbering of the compounds corresponds to that of the original acids except in the case of substituted amides).

We synthesized amides of 2-carboxyethyl ethers of acetylenic alcohols (Tables 4 and 5) with the object of testing their physiological activity, particularly in connection with the search for new soporifics, it being noteworthy that data have recently appeared in the literature concerning the soporific action of certain acetylenic alcohols and their derivatives [5].

TABLE 2

Compound	Found (%)		Calculated (%)		Molecular weight	
	C	H	C	H	Found	Calculated
I	61.30 61.35	7.95 7.77	61.54	7.69	160.8 160	156
II					168 172.2	170
III					170 172.7	170
IV	60.93 70.78	7.94 7.84	61.54	7.69	157 158.2	156
V					172.1 172.8	170
VI					185 184.7	184
VII					233.7 229.4	226
VIII					255.9 259	254
IX					185.8 183.2	184
X					215.5 212.7	212
XI					213.9 217	212
XII	65.43 65.49	7.73 7.71	65.93	7.68	184.1 184.1	182
XIII	67.23 67.21	8.37 8.31	67.34	8.16	192.2 192.1	196
XIV					214.7 216.7	210
XV	71.96 71.84	9.00 8.86	72.0	8.80	260.4 261	250
XVI	63.21 63.14	8.05 8.07	63.71	8.00	230.7 232.5	226

EXPERIMENTAL

Hydrolysis of the previously described [2] 2-(methoxycarbonyl)ethyl ethers of acetylenic alcohols, and also the conversion of the resulting acids into acid chlorides and amides, was carried out by a standard procedure, which will now be described for the case of the 2-(methoxycarbonyl)ethyl ether of 2-methyl-3-butyn-2-ol.

Hydrolysis of the 2-(Methoxycarbonyl)ethyl Ether of 2-Methyl-3-butyn-2-ol.

To a solution of 25 g of sodium hydroxide in 25 ml of water and 475 ml of methanol, 17 g of the 2-(methoxycarbonyl)ethyl ether of 2-methyl-3-butyn-2-ol (b.p. 83-84°, 12 mm) [2] was added. After careful stirring, the mixture was left for 20 hours at room temperature. A current of carbon dioxide was then passed through the mixture for 90 minutes in order to neutralize the alkali, the precipitate formed was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue and the precipitate on the filter were dissolved in water, and the aqueous solution was subjected to extraction by ether, was acidified to Congo red with hydrochloric acid, and was saturated with sodium chloride. The solution was extracted with three portions of ether, and the ether extract was dried with magnesium sulfate and vacuum-fractionated. The product, amounting to 14 g was the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV), b.p. 108-110° (3.5 mm); n_D^{20} 1.4419; d_4^{20} 1.0263; found MR 40.21; calculated MR 40.26; found M 157, 158.2 (by titration); calculated M 156.

Found %: C 60.93; 60.78; H 7.94; 7.84. $C_9H_{12}O_3$. Calculated %: C 61.54; H 7.69.

The 2-carboxyethyl ethers of the other acetylenic alcohols (Table 1) were prepared similarly.

Alkaline Hydrolysis of the 2-Cyanoethyl Ether of 2-Methyl-3-butyn-2-ol

a) A mixture of 10 g of the 2-cyanoethyl ether of 2-methyl-3-butyn-2-ol (b.p. 96-97°, 18 mm) [6], 15 g of potassium hydroxide, and 100 ml of water was stirred at 50-60° for 15 hours. The cooled mixture was acidified with hydrochloric acid, and the acid solution was saturated with sodium chloride. The solution was then extracted with three portions of ether, and the ether extracts were dried with magnesium sulfate. Vacuum fractionation gave 2.1 g of the 2-carboxyethyl ether (IV), b.p. 104-107° (3 mm) and n_D^{20} 1.4406.

b) A mixture of 10 g of the 2-cyanoethyl ether of 2-methyl-3-butyn-2-ol, 12 g of potassium hydroxide, 50 ml of methanol, and 50 ml of water was boiled for 20 hours. Methanol was distilled off under reduced pressure, and the aqueous residue was acidified with hydrochloric acid, saturated with sodium chloride, and extracted with three portions of ether. The ether extracts were dried with magnesium sulfate. Vacuum distillation gave 4.5 g of 3-methoxypropionic acid, b.p. 96-97° (7 mm) and n_D^{20} 1.4208.

c) A mixture of 10 g of the 2-cyanoethyl ether of 2-methyl-3-butyn-2-ol, 8 g of potassium hydroxide, and 100 ml of methanol was boiled for 35 hours. Alkali was neutralized with hydrochloric acid, methanol was distilled off, and the residue was acidified with hydrochloric acid and extracted with three portions of ether. The ether extracts were dried with magnesium sulfate. Vacuum fractionation gave 3.1 g of the 2-carboxyethyl ether (IV), b.p. 112-115° (5 mm) and n_D^{20} 1.4397.

Reaction of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol (IV) with Diazomethane.

An ethereal solution of diazomethane was prepared from 5 g of 1-nitroso-1-methylurea, 15 ml of 40% aqueous potassium hydroxide, and 50 ml of ether, and 5.2 g of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) (b.p. 116-118°, 6 mm) was added gradually at 5°. The ether layer was separated, dried with magnesium sulfate, and vacuum-fractionated. The product, amounting to 5.6 g, was the 2-(methoxycarbonyl)ethyl ether of 2-methyl-3-butyn-2-ol, b.p. 85-87° (16 mm) and n_D^{20} 1.4296.

Preparation of the Acid Chloride of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol

A mixture of 26.5 g of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) (b.p. 108-110°, 3.5 mm) and 21 ml of thionyl chloride was heated under reflux at 50-60° in a round-bottomed flask for 1.5-2 hours. Vacuum fractionation of the product gave 28.2 g of the acid chloride, b.p. 85-87° (24 mm); n_D^{20} 1.4432; d_4^{20} 1.0510; found MR 43.94; calculated MR 43.97.

The acid chlorides of the other 2-carboxyethyl ethers of acetylenic alcohols were prepared similarly (Table 3).

Reaction of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol with Thionyl Chloride in presence of Pyridine

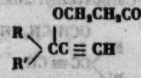
a) A solution of 2.4 g (0.02 mole) of thionyl chloride in 10 ml of dry ether was added in small portions at −5° to a stirred cooled solution of 3.12 g (0.02 mole) of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol and 1.6 g (0.02 mole) of pyridine in 10 ml of dry ether. The mixture was left for one hour at room temperature, ether was distilled off, and the product was vacuum fractionated, yielding 1 g of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV), b.p. 85-86° (24 mm) and 2.1 g of the corresponding anhydride, b.p. 155-157° (3.5 mm); n_D^{20} 1.4518; d_4^{20} 1.0361; found MR 76.52; calculated MR 75.91

Found %: C 64.45; 64.37; H 7.52; 7.48. $C_{18}H_{22}O_5$. Calculated %: C 65.30; H 7.48.

b) A mixture of 3.12 g (0.02 mole) of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol, 1.6 g (0.02 mole) of pyridine, and 2.4 g (0.02 mole) of thionyl chloride in 20 ml of dry ether was left at room temper-

TABLE 3

Acid Chlorides of 2-Carboxyethyl Ethers of Acetylenic Alcohols



Original acid	Acid chlorides					
	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated
I	94	65—67(3,5)	1.4471	1.0832	43.73	43.97
II	96	88—90(8)	1.4509	1.0560	47.91	48.59
III	96	72—74(4)	1.4476	1.0397	48.37	48.59
IV	95	85—87(24)	1.4432	1.0510	43.94	43.97
V	98	75—77(6)	1.4479	1.0355	48.59	48.59
VI	99	85—87(6)	1.4493	1.0471	52.79	53.20
VII	97	122—124(6)	1.4531	0.9868	66.84	67.06
VIII	92	147—149(4)	1.4551	0.9606	76.73	76.30
IX	97	80—82(5)	1.4508	1.0347	52.54	53.20
X	97	98—100(3,5)	1.4546	1.0058	62.00	62.44
XI	94	95—97(4)	1.4630	1.0226	61.95	62.44
XII	95	91—93(4)	1.4753	1.1101	50.75	51.00
XIII	97	112—114(6)	1.4900	1.0896	55.79	55.62
XIV	94	109—111(3,5)	1.4764	1.0748	60.06	60.24
XV	89	152—154(4)	1.5010	1.0916	72.33	71.90
XVI	94	127—129(5)	1.4782	1.1215	61.70	61.88

ature, for 18 hours, and 2.8 g of the corresponding anhydride, b.p. 155-157° (3.5 mm) was obtained.

Preparation of the Amide of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol

Dry ether (50 ml) was placed in a three-necked flask fitted with mechanical stirrer having a glycerol seal, dropping funnel, and tube for passage of gas, which reached almost to the bottom of the flask. The ether was stirred and cooled with ice water while ammonia gas was passed to saturation, and a solution of 7 g of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) in 30 ml of dry ether was added at 0° over a period of 90 minutes with continuous passage of ammonia gas. The reaction mixture was then stirred at room temperature for a further 90 minutes, and the precipitated ammonium chloride was then filtered off and washed on the filter with ether. The ether solutions were combined, and ether was distilled off under reduced pressure. The residue was dissolved in dry ether and reprecipitated with petroleum ether. The product (6.25 g) was the amide, m.p. 51-52.5°.

Found %: N 9.15; 9.17; C 61.47; 61.59; H 8.37; 8.50. $C_9H_{15}NO_3$. Calculated %: N 9.03; C 61.93; H 8.38.

All the other amides of 2-carboxyethyl ethers of acetylenic alcohols were prepared by this method (Table 4).

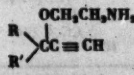
Preparation of the Methylamide of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol (XVII)

A solution of 8.7 g (0.05 mole) of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) in 30 ml of dry ether was added over a period of two hours to a stirred cooled (ice water) solution of 3.2 g (0.1 mole) of methylamine in 25 ml of methanol contained in a three-necked flask. The mixture was stirred at the room temperature for two hours, and methylamine hydrochloride was filtered off and washed on the filter with ether. Ether and methanol were removed under reduced pressure. Vacuum fractionation of the residue gave 8.4 g of the methylamide (XVII), b.p. 133-137° (5 mm); n_D^{20} 1.4622; d_4^{20} 1.0002.

Found %: N 8.09; 8.12. $C_9H_{15}NO_3$. Calculated %: N 8.28.

TABLE 4

Unsubstituted Amides of 2-Carboxyethyl Ethers of Acetylenic Alcohols



Original acid	Amides					M. p. (°C)
	Yield (%)	B.p. in (°C) (p in mm)	n_D^{20}	Found N (in %)	Calculated (in %)	
I	98	147—149(4)	1.4711	8.67 8.45	9.03	—
II	99	158—161(4)	1.4661	7.97 8.10	8.28	—
IV	100	—	—	9.15 9.17	9.03	51—52.5*
V	98	153—154(6)	1.4710	8.70 8.99	8.28	—
VI	100	154—156(4)	1.4680	7.62 7.51	7.65	—
VII	98	179—181(4)	—	6.17 6.15	6.22	—
IX	98	153—156(4)	1.4703	7.91 8.10	7.65	—
X	100	169—172(5)	1.4699	6.26 6.45	6.63	—
XII	100	—	—	7.94 7.80	7.74	57—58*
XIII	100	—	—	7.59 7.50	7.18	71—72**
XV	99	—	—	5.39 5.37	5.62	75.5—77***
XVI	99	194—196(4)	—	6.55 6.64	6.62	-

* From ether by precipitation with petroleum ether.

** From cyclohexane.

*** From a mixture of isooctane and benzene.

The methylamide (XXI) was prepared in the same way (Table 5).

Preparation of the Dimethylamide of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol (XVIII)

Gaseous dimethylamine (4.5 g, i.e. 0.1 mole) was passed into a stirred cooled (ice water) solution of 5g (0.03 mole) of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) over a period of two hours. The reaction mixture was stirred at room temperature for two hours, and dimethylamine hydrochloride was filtered off and washed with ether. After removal of ether, the product was vacuum fractionated and gave 5.1 g of the dimethylamide (XVIII), b.p. 117-121° (5 mm); n_D^{20} 1.4630; d_4^{20} 0.9863.

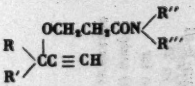
Found % N 7.75; 7.83. $C_{10}H_{17}NO_3$. Calculated % N 7.65.

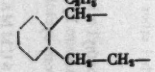
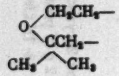
Preparation of the Diethylamide of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol (XIX)

A solution of 5 g (0.03 mole) of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) in 25 ml of dry ether was added to a stirred cooled (ice water) solution of 5 g (0.07 mole) of diethyl-

TABLE 5

Substituted Amides of 2-Carboxyethyl Ethers of Acetylenic Alcohols



Compound	R	R′	R″	R‴	Yield	B.p. in °C (p in mm)	M.p. (°C)	n_D^{20}	Found N (in %)	Calculated N (in %)
XVII	CH_3	CH_3	CH_3	H	99	133—137 (5)	—	1.4622	8.09 8.12	8.28
XVIII	CH_3	CH_3	CH_3	CH_3	97	117—121 (5)	—	1.4630	7.75 7.83	7.65
XIX	CH_3	CH_3	C_2H_5	C_2H_5	97	127—131 (5)	—	1.4575	6.90 6.69	6.63
XX	CH_3	CH_3	$(CH_2)_5$		98	154—157 (5)	—	1.4870	6.55 6.59	6.28
XXI		$(CH_2)_5$	CH_3	H	98	170—173 (5)	—	1.4914	6.22 6.53	6.70
XXII	CH_3	CH_3	C_6H_5	H	96	—	87—88*	—	6.42 6.64	6.06
XXIII	CH_3	C_2H_5	C_6H_5	H	97	—	54—55*	—	5.92 5.89	5.71
XXIV		$(CH_2)_5$	C_6H_5	H	98	—	74.5—76*	—	5.43 5.33	5.16
XXV	C_2H_5	H	C_6H_5	H	100**	—	—	—	—	—
XXVI			C_6H_5	H	100**	—	—	—	—	—
XXVII			C_6H_5	H	100**	—	—	—	—	—

* From a mixture of isooctane and benzene.

** Cannot be distilled, and crystallizes with great difficulty.

amine in 25 ml of dry ether over a period of 90 minutes. The mixture was then stirred at room temperature for two hours. Diethylamine hydrochloride was filtered off and washed with ether. After removal of ether, the product was vacuum-fractionated and gave 5.9 g of the diethylamide (XIX), b.p. 127-131° (5 mm); n_D^{20} 1.4575; d_4^{20} 0.9584.

Found %: N 6.90; 6.69. $C_{12}H_{21}NO_2$. Calculated %: N 6.63.

Preparation of the Piperidide of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol (XX)

A solution of 5 g (0.03 mole) of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) in 25 ml of dry ether was added to a stirred cooled (ice water) solution of 5.5 g (0.065 mole) of piperidine in 25 ml of dry ether over a period of two hours. The mixture was then stirred at room temperature for one hour. Piperidine hydrochloride was filtered off and washed with ether. After removal of ether, the product was vacuum fractionated and gave 6.3 g of the piperidide (XX), b.p. 154-157° (5 mm); n_D^{20} 1.4870.

Found %: N 6.55; 6.59. $C_{13}H_{21}NO_2$. Calculated %: N 6.28

Preparation of the Anilide of the 2-Carboxyethyl Ether of 2-Methyl-3-butyn-2-ol (XXII)

A solution of 5 g (0.03 mole) of the acid chloride of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV) in 25 ml of dry ether was added over a period of one hour to a solution of 6 g (0.064 mole) of aniline in 25 ml of dry ether with stirring and cooling with ice water. The mixture was then stirred at room temperature for 2 hours 30 minutes, aniline hydrochloride was filtered off and washed with ether, and ether was distilled off under reduced pressure. The product, amounting to 6.4, was the anilide (XXII), m.p. 87-88° (from a mixture of isooctane and benzene).

Found %: N 6.42; 6.64. $C_{14}H_{17}NO_2$. Calculated %: N 6.06.

All the other anilides described in Table 5 were synthesized similarly.

Hydrolysis of 2-Cyanoethyl Ethers of Acetylenic Alcohols with Alkaline Hydrogen Peroxide

a) A solution of 1.5 g of potassium hydroxide in 200 ml of 5% hydrogen peroxide was prepared in a three-necked flask fitted with mechanical stirrer, dropping funnel, and thermometer. The solution was stirred vigorously while 13.5 g of the 2-cyanoethyl ether of 2-methyl-3-butyn-2-ol (b.p. 96-97°, 18 mm) [6] was added at such a rate that the temperature of the mixture did not rise above 40°. When the whole of the 2-cyanoethyl ether had been added, the reaction mixture was stirred at 45-50° for three hours, in the course of which the solution became quite clear. The solution was saturated with potassium carbonate and extracted with ethyl acetate. The solution of the product in ethyl acetate was dried with magnesium sulfate, and ethyl acetate was distilled off in the vacuum of a water pump at a temperature of not above 40°. The product was dissolved in dry ether and precipitated with petroleum ether. The amide of the 2-carboxyethyl ether of 2-methyl-3-butyn-2-ol (IV), amounting to 13.4 g, melted at 49-51°.

b) Similarly, from 10 g of the 2-cyanoethyl ether of 1-ethynylcyclohexanol (b.p. 92-95°, 3 mm) [7], 250 ml of 5% hydrogen peroxide, and 2 g of potassium hydroxide, 9.8 g of the amide of the 2-carboxyethyl ether of 1-ethynylcyclohexanol (XIII), m.p. 68-71° (from cyclohexane), was obtained.

SUMMARY

1. In acid hydrolysis 2-cyanoethyl ethers of acetylenic alcohols are almost completely resinified, and in alkaline hydrolysis the expected 2-carboxyethyl ethers of acetylenic alcohols are obtained, but in poor yield (30-40%).

2. 2-Carboxyethyl ethers of acetylenic alcohols are formed smoothly and in good yield (76-94%) by the hydrolysis of the readily accessible 2-(methoxycarbonyl) ethyl ethers of acetylenic alcohols by treatment with

aqueous-methanolic sodium hydroxide at room temperature.

3. In order to be able to test their physiological, particularly soporific, activities, some amides of 2-carboxyethyl ethers of acetylenic alcohols were synthesized by the action of ammonia or amines on the corresponding acid chlorides.

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* T.p. = C. B. Translation pagination.

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FREE-RADICAL POLYMERIZATION AND COPOLYMERIZATION OF 2-BUTOXYETHYL VINYL SULFIDE

M. F. Shostakovsky, E. N. Prilezhaeva, and A. M. Khomutov

There has been some interest in the synthesis of polymers containing sulfur. It has been shown, for example, that the introduction of sulfone groups improves the gasoline-resistance of polymers [1] and that the presence of sulfide sulfur improves dielectric properties [2] and makes the polymer thermoplastic [3]. A comparatively little studied source for the preparation of sulfur-containing polymers is formed by alkyl vinyl sulfides. It is stated in patents [3] that ethyl vinyl sulfide, and also various aryl vinyl sulfides, can yield polymers under the influence of light and in presence of catalysts such as peroxides, Friedel-Crafts catalysts, sulfur dioxide, etc. However, in Scheidknecht's review [4] it is justifiably stated that, for practical purposes, the polymerization characteristics for compounds of this class remain uncertain. Since then, two of the authors of the present paper have shown that ethyl vinyl sulfide and 2-butoxyethyl vinyl sulfide polymerize slowly under the action of light and atmospheric oxygen [5, 6] and 2-butoxyethyl vinyl sulfide gives a fairly high yield of polymer when heated with 2,2'-azobis[2-methylpropionitrile] [5]. As regards copolymerization reactions, recommendations have been made that benzoyl peroxide should be used in the copolymerization of alkyl vinyl sulfides with acrylonitrile [7] and also in the copolymerization of methyl vinyl sulfide with methyl acrylate and with styrene [8]. The yields of the acrylonitrile copolymers are not given, but in the copolymerizations with methyl methacrylate and with styrene the process came to an end at a progress of reaction of 10-20%.

From a comparison of these isolated results with data on the behavior of alkyl vinyl sulfides in other addition reactions [6, 9, 10] we may infer that, in spite of the considerable nucleophilic character of the double bonds in alkyl vinyl sulfides, these sulfur compounds are more reactive toward free radicals and less active toward ions than their oxygen analogs, the vinyl ethers. We therefore undertook a more systematic investigation of the free-radical polymerization reactions of alkyl vinyl sulfides.

In the present investigation we studied the polymerization and copolymerization of 2-butoxyethyl vinyl sulfide, which we synthesized from butyl vinyl sulfide by the method already developed [5, 11]:

$$CH_2{=}CHOC_4H_9 + H_2S \rightarrow CH_2SH - CH_2OC_4H_9 + CH \equiv CH \rightarrow CH_2{=}CHSCH_2CH_2OC_4H_9$$

As the second component in copolymerization we took methyl methacrylate, which has been studied previously in copolymerization with various vinyl ethers [12, 13].

Two initiators were used - benzoyl peroxide and 2,2'-azobis[2-methylpropionitrile]. It was shown that, in the polymerization of 2-butoxyethyl vinyl sulfide, benzoyl peroxide is a considerably less active initiator than the azo dinitrile this being evidenced not only in the yield of polymer, but also in its molecular weight (Table 1). In presence of the dinitrile, polymers of somewhat greater molecular weight are formed in considerably higher yields than in the case of vinyl ethers under the same conditions. The polymers are very viscous liquids, soluble in most organic solvents apart from the lower alcohols. In the freshly purified form the polymers are free from odor, but after prolonged keeping in presence of air a feeble odor of the original thiol appears.

Like the polymerization experiments, the experiments on the copolymerization of 2-butoxyethyl vinyl sulfide with methyl methacrylate were carried out at 60° in presence of 0.2% of initiator. At higher concentrations of initiator (Table 2) and at lower temperatures (Table 3) the yield of copolymer was appreciably less.

TABLE 1

Polymerization of 2-Butoxyethyl Vinyl Sulfide
(reaction temperature 60°, initiator concentration 0.2%)

Initiator	Duration of heating (hours)	Yield of polymer (%)	Molecular weight of * polymer
Benzoyl peroxide	80	11.6	2000-2500
2,2'-Azobis [2-methyl-propionitrile]	24	42.0	–
	48	48 – 50	–
	96	65 – 68	~10,000

* Determined cryoscopically.

TABLE 2

Effect of the Bz_2O_2 Concentration on the Yield of Copolymers of Methyl Methacrylate (M_1) and 2-Butoxyethyl Vinyl Sulfide (M_2) (equimolecular proportions, 96 hours at 60°, total weight 10 g)

Bz_2O_2 concentration (%)	Yield of copolymer (% on weight of monomers)	Composition of copolymer	
		S found (%)	Mole % of M_2
0.1	35.6	9.69	35.6
0.2	29.7	10.03	38.7
1.0	24.7	10.11	39.0

TABLE 3

Effect of Temperature on the Copolymerization of 2-Butoxyethyl Vinyl Sulfide with Methyl Methacrylate $M_1 : M_2$ (mole %) = 61.5 : 38.5; dinitrile 0.2%; total weight 5 g

Polymerization conditions		Yield of copolymer (% on weight of monomers	Composition of copolymer	
Temperature (°C)	Time (hours)		S found (%)	Mole % of M_2
40	100	84.4	9.3	35.2
60	24	85.2	8.9	32.6
90*	40	45.6	8.2	30.3

* The polymer turned yellow.

The yield of copolymers are shown graphically in Fig. 1 as a function of the composition of the mixture of monomers for both of the initiators used. The dinitrile, being the more active initiator, gives copolymers in yields of up to 80-90%.

In Fig. 2, the compositions of the copolymers – in their relationship to the composition of the mixture of monomers – are compared with the data obtained by two authors of this paper for copolymers of methyl methacrylate with vinyl ethers [12, 13]. In accord with its higher reactivity toward free radicals of the other monomer, the vinyl sulfide is drawn into the copolymer to a much greater degree than an alkyl vinyl ether.

The yield of 2-butoxyethyl vinyl sulfide copolymer falls as we pass from mixtures of monomers having a high methyl methacrylate content to mixtures containing a smaller proportion of this component. There is a simultaneous increase in the mole fraction of sulfur-containing units in the copolymer. It will be clear that the most probable mechanism for the initiation of the polymer chain is the formation of a free radical from methyl methacrylate $RCH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}$, in which R is a radical initiator, with subsequent participation of vinyl sulfide and methyl methacrylate molecules in the process*. It will be seen from Table 4 that copolymer formed in the early stages of the process is somewhat enriched in methyl methacrylate, although a stationary composition is rapidly established.

* The reverse order is not, of course, completely excluded.

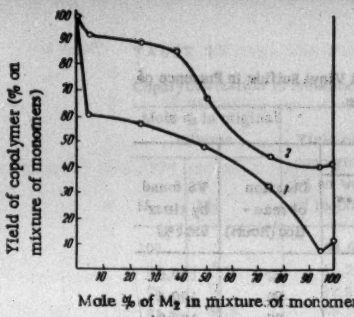

Fig. 1. Yields of copolymers of methyl methacrylate (M_1) and 2-butoxyethyl vinyl sulfide (M_2) obtained: 1) with Bz_2O_2 (80 hours at 60°); 2) with dinitrile (24 hours at 60°).

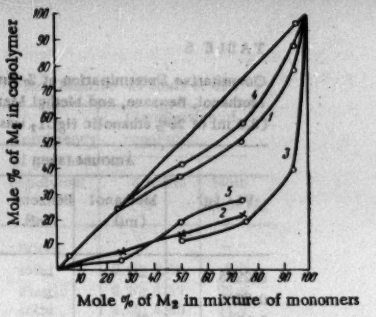

Fig. 2. Compositions of copolymers of methyl methacrylate (M_1) with vinyl sulfides or vinyl ethers (M_2): 1) Bz_2O_2; $M_2 = CH_2 = CHSCH_2CH_2OC_4H_9$; 2) Bz_2O_2; $M_2 = CH_2 = CHOC_2H_5$; 3) Bz_2O_2; $M_2 = CH_2 = CHOC_4H_9$-t; 4) dinitrile; $M_2 = CH_2 = CHSCH_2CH_2OC_4H_9$; 5) dinitrile; $M_2 = CH_2 = CHOC_4H_9$ t.

The copolymers obtained vary in physical properties; thus they range from brittle solids, through plastic solids, to viscous, sticky masses (with high sulfur content). The copolymers are soluble in most organic solvents, except the lower alcohols. Unlike polymethyl methacrylate, copolymers containing more than 5 mole % of vinyl sulfide units are readily soluble in ether and in a mixture of butyl alcohol and butyl vinyl ether. The dependence of the viscosities of the copolymers on their composition and method of preparation is shown in Fig. 3.

TABLE 4

Yields of Compositions of Copolymers Obtained from an Equimolecular Mixture (reaction temperature 60°; Bz_2O_2 0.2% total weight 5.0 g)

Time (hours)	Yield of copolymer (% weight of monomers)	Mole % of M_2 in copolymer
2	10.2	35.0
4	18.6	35.0
8	24.4	37.5
30	42.0	37.5
54	45.6	37.5
80	47.6	37.5
96	50.6	37.5

The course of the polymerization or copolymerization process can be readily followed by titration of unchanged vinyl sulfide by the acidometric method suggested previously [5]; this is based on the reaction:

$$RSCH=CH_2 + HgCl_2 + 2C_2H_5OH \rightarrow RSHgCl + HCl + CH_3CH(OC_2H_5)_2.$$

EXPERIMENTAL*

The monomers were freshly distilled for use. Benzoyl peroxide was reprecipitated from chloroform with methanol, and commercial 2,2'-azobis[2-methylpropionitrile] was recrystallized twice from methanol. The reactions were carried out in sealed tubes, 15-20 ml in capacity; these were placed in a water thermostat, temperature 60 ± 1°. The total weight of monomers was 5 g in most of the experiments. The copolymers were dissolved in the least possible amount of benzene (10-20 ml) and precipitated with 150-160 ml of dry methanol. This was repeated, and the copolymers were then dried at 60°. In order to determine unchanged vinyl sulfide, sulfide, after the reprecipitations the total volume of solvent was measured, and an excess of 20% ethanolic mercuric chloride was added to an aliquot (10-20 ml). After 48 hours, the acid liberated was titrated with standard sodium hydroxide solution. The results of preliminary experiments on artifically prepared mixtures (Table 5) showed that, under these conditions of analysis, the presence of benzene and methyl methacrylate did not interfere with the determination of the vinyl sulfide.

By way of example, we give the reaction balance sheet for one of the experiments. The amounts taken were M_1 – 1.92 g and M_2 – 3.08 g (1:1 ratio); copolymerization for 80 hours at 60° (initiator Bz_2O_2).

* L. V. Tsymbal took part in the experimental work.

TABLE 5

Quantitative Determination of 2-Butoxyethyl Vinyl Sulfide in Presence of Methanol, Benzene, and Methyl Methacrylate
(3.5 ml of 20% ethanolic $HgCl_2$ was added)

Amount taken				Duration of reaction (hours)	VS found by titration (%)
VS* (g)	Methanol (ml)	Benzene (ml)	MMA** (ml)		
0.2215	–	–	–	20	100.0
0.2201	–	–	–	20	100.4
0.1880	20	–	–	20	100.0
0.2134	20	–	–	20	99.9
0.2162	15	5	–	20	99.4
0.2396	15	5	–	20	100.4
0.2342	14	5	1	20	95.7
0.2242	14	5	1	20	97.9
0.2015	14	5	1	48	100.2
0.2175	14	5	1	48	99.5

* VS=vinyl sulfide
** MMA=methyl methacrylate

Amount of copolymer obtained – 2.38 g (47.6%).

Found (%): C 59.70; 59.76; H 9.08; 9.01; S 9.70; 9.76.. Calculated mole % of M_2 in copolymer: 37.3%. Found by titration: M_2 1.77 g (unchanged in reaction). Total M_2 found (taking account of that entering into the reaction): 2.96 g (97.2% of original amount taken).

Tables 6 and 7 present data on the consistency, yield, and analysis of copolymers obtained in presence of Bz_2O_2 and of dinitrile, and Table 8 gives the solubilities of some copolymers in mixtures of butyl vinyl ether and butyl alcohol.

TABLE 6

Copolymerization in Presence of 0.2% of Benzoyl Chloride (80 hours, 60°)

Mole % in original mixture		Yield of copolymer (% on weight of monomers)	Consistency of purified copolymer	Composition of copolymer *	
M_1	M_2			S found (%)	Mole % of M_2
100	–	99.6	Brittle solid	–	–
95	5	60.6		1.68; 1.61	4.7
75	25	56.8	Plastic solid	6.72; 6.66	23.3
50	50	47.6		9.70; 9.76	37.3
25	75	32.7		12.40; 12.39	50.5
5	95	7.4	Viscous liquid	16.56; 16.38	78.5
–	100	11.6		19.78; 19.85	100

* Analyses for C and H were not carried out since the monomers have almost the same carbon content.

TABLE 7

Copolymerization in Presence of 0.2% of the Dinitrile 24 hours at 60°)

Mole % in original mixture		Yield of copolymer (% on weight of monomers)	Consistency of purified copolymer	Composition of copolymer	
M_1	M_2			S found (%)	Mole % of M_2
100	—	98.0	Brittle		—
95	5	91.2	solid	2.42; 2.48	5.3
75	25	87.6	Plastic	6.76; 6.57	23.9
61,5	38.5	85.2	solid	8.98; 8.83	34.4
50	50	67.0		10.47; 10.52	40.8
25	75	44.0		13.82; 13.60	57.8
5	95	41.0	Viscous	18.51; 18.34	88.0
—	100	42.0	liquid	19.78; 19.85	100

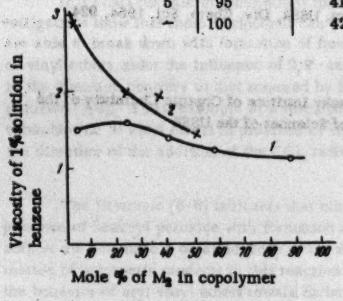

Fig. 3. Viscosities of copolymers of 2-butoxyethyl vinyl sulfide and methyl methacrylate prepared 1) with dinitrile; and 2) with Bz_2O_2.

TABLE 8

Solubilities of Copolymers

Composition of polymer or copolymer (mole %)		Amount of (co) polymer taken (g)	Amount of butyl alcohol (ml)	Amount of butyl vinyl ether (ml)	Characteristics of solution
M_1	M_2				
100	—	0.20	15	28.0	0.2 g of precipitate
94.7	5.3	0.20	15	32.6	0.2 g of precipitate
76.1	23.9	0.20	10	6.9	Clear solution
65.6	34.4	0.20	10	5.58	Ditto
59.2	40.8	0.20	10	2.9	» »
	100	0.20	10	—	» »

SUMMARY

1. It was shown that, in free-radical homopolymerization and copolymerization, 2-butoxyethyl vinyl sulfide is more reactive than vinyl ethers.

2. It was shown that 2,2'-azobis[2-methylpropionitrile] is a more reactive initiator in the reactions studied than benzoyl peroxide. In presence of the dinitrile, homopolymers of 2-butoxyethyl vinyl sulfide were prepared in yields of up to 65-68%, and its copolymers with methyl methacrylate were prepared in yields of up to 70-90%.

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OLIGOMERIZATION

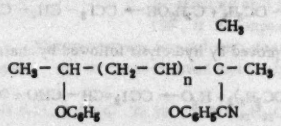
COMMUNICATION 1. REACTION OF SOME VINYL ETHERS WITH CARBON TETRACHLORIDE

M. F. Shostakovsky, A. V. Bogdanova, M. M. Zverov, and G. I. Plotnikova

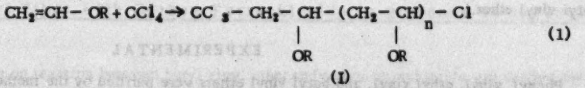
It is characteristic of vinyl ethers that they tend to react by an ionic mechanism. However, recent investigations show that these compounds can be caused to take part also in reactions initiated by reagents that are able to break down with formation of free radicals. Examples are the polymerization and copolymerization of vinyl ethers under the influence of 2,2'-azobis[2-methylpropionitrile] [1], the addition of thiols to vinyl ethers in the direction contrary to that required by Markovnikov's rule [2], and the reaction of vinyl ethers with benzoyl peroxide [3,4]. A new example of a reaction that proceeds by a free-radical mechanism is the addition of carbon tetrachloride to vinyl ethers in presence of benzoyl peroxide. This reaction affords the possibility of studying the direction of the addition of the $\dot{C}Cl_3$ radical and Cl atom formed from carbon tetrachloride [5].

The literature [6-8] indicates that ethyl vinyl and butyl vinyl ethers react with carbon tetrachloride in presence of benzoyl peroxide with formation of ethyl tetrachloropropyl and butyl tetrachloropropyl ethers. The authors did not make a detailed study of the conditions for reaction and the question of the possibility of the formation of polymeric products in this reaction remains obscure. There is no information in the literature about the behavior of aryl vinyl ethers toward carbon tetrachloride in presence of benzoyl peroxide and their possible polymerization under these conditions.

Our study of the polymerization of phenyl vinyl ether in presence of 2,2'-azobis[2-methylpropionitrile] [1] showed that, under certain conditions, telomeric products of the type



may be formed. It might be expected, therefore, that again in the reaction of phenyl vinyl ether with carbon tetrachloride in presence of benzoyl peroxide, products of low molecular weight would be formed in accordance with the scheme:



(1)

(I)

A similar reaction occurs between vinyl acetate and carbon tetrachloride and has been described in a patent [9].

The present paper is devoted to an examination of the conditions under which phenyl vinyl, butyl vinyl, and ethyl vinyl ethers react with carbon tetrachloride in presence of benzoyl peroxide and to a study of some of the properties of the products. The experiments showed that, depending on the conditions, phenyl vinyl and alkyl vinyl ethers may react with carbon tetrachloride with formation of the products of equimolecular addition:

$$CH_2=CH-OR + CCl_4 \rightarrow \underset{(II)}{CCl_3-CH_2-CHCl-OR} \quad (2)$$

(R=C_2H_5, C_4H_9, or C_6H_5) or of polymeric products by Equation 1. By variation of reaction conditions (temperature, amount of catalyst, relative amounts of reactants and the order of mixing, carrying out the reaction in a flask with stirrer or in a sealed tube), it was possible to find optimum conditions for the formation of equimolecular-addition products or of polymeric products. Equimolecular-addition products (II) were obtained in good yield when the relative amounts of vinyl ether and CCl_4 were 1:4 and 1:2. In this case it is best to carry out the reaction in a flask fitted with stirrer, adding the vinyl ether dropwise to the carbon tetrachloride. With increase in the amount of vinyl ether the yield of the tetrachloropropyl ether falls, but the amount of polymeric product rises.

The resulting phenyl 1,3,3,3-tetrachloropropyl ether and alkyl 1,3,3,3-tetrachloropropyl ethers are substituted α-chloro ethers, the properties of which we have studied previously [10]. Their structure was proved by hydrolytic scission, carried out under various conditions. Such scission probably occurs in the following way:

$$CCl_3-CH_2-CHCl-OR + H_2O \rightarrow [CCl_3-CH_2-CHO] + ROH + HCl \quad (3)$$

$$[CCl_3-CH_2-CHO] \rightarrow CCl_2=CH-CHO + HCl \quad (4)$$

Experiment showed that it is not possible to separate the two stages (3) and (4) of the hydrolysis of tetrachloropropyl ethers owing to the instability of trichloropropionaldehyde. The quantitative formation of phenol and dichloroacrolein, which is observed when the phenyl tetrachloropropyl ether is boiled with water for one hour, corresponds to the elimination of two molecules of hydrogen chloride from one molecule of the tetrachloro ether.

When the phenyl tetrachloropropyl ether is heated to 100° with alkali, elimination of hydrogen chloride may proceed further to the stage of chloroacetylene, so that a slight explosion occurred when the tube was opened and the hydrolyzate showed a positive reaction for acetylene. Quantitative determinations were made for hydrogen chloride, phenol, and dichloroacrolein on hydrolyzates obtained under various conditions. Hydrogen chloride was determined by titration with 0.1 N NaOH, phenol was determined gravimetrically as tribromophenol, and dichloroacrolein was characterized as its semicarbazone. The mobility of α-chloro in tetrachloropropyl ethers was shown by its replacement by an alkoxy group with formation of the diethyl acetal of 3,3,3-trichloropropionaldehyde (III):

$$CCl_3-CH_2-CHCl-OC_2H_5 + C_2H_5OH \rightarrow CCl_3-CH_2-CH(OC_2H_5)_2 + HCl \quad (5)$$

The structure of the acetal obtained was proved by hydrolysis followed by characterization of dichloroacrolein:

$$CCl_3-CH_2-CH(OC_2H_5)_2 + H_2O \rightarrow CCl_2=CH-CHO + 2C_2H_5OH + HCl \quad (6)$$

The polymeric products of the addition of vinyl ethers to carbon tetrachloride, the yield of which rises with increase in the proportion of vinyl ether in the original mixture, were found to be colorless or feebly colored transparent substances – viscous liquids in the case of alkyl vinyl ethers, and solids in for phenyl vinyl ether. Investigation of their compositions showed that in these polymeric products there are 4-5 monomer molecules per CCl_4 molecule in the case of phenyl vinyl ether and 41 monomer molecules per CCl_4 molecule in the case of butyl vinyl ether.

EXPERIMENTAL

Phenyl vinyl, ethyl vinyl, and butyl vinyl ethers were purified by the method developed in the Vinylic Compounds Laboratory [11] and had the following constants: phenyl vinyl ether, b.p. 155-156°, n_D^{20} 1.5223; d_4^{20} 0.9770; ethyl vinyl ether, b.p. 36-36.5°, n_D^{20} 1.3780; d_4^{20} 0.7530; butyl vinyl ether, b.p. 93-94°, n_D^{20} 1.4030; d_4^{20} 0.7790. Carbon tetrachloride was distilled, washed four times with water, dried over calcium chloride, and redistilled (b.p. 76-76.5°). Benzoyl peroxide was purified by reprecipitation with methanol from chloroform solution; it was dried to constant weight in a vacuum desiccator [12].

TABLE 1

Reaction of Vinyl Ethers (VE) with Carbon Tetrachloride

No.	Molecular ratio VE : CCl_4	Maximum reaction temperature (°C)	Amt. obtained: Tetrachloroether (% of theoretical)	Amt. obtained: Polymeric product (% on orig. mix.)	Vinyl ether
1	1:4	75	95.3	2.0	
2	1:3	85	88.5	5.5	
3	1:2	95	80.1	7.7	
4	1:1	115	69.4	23.6	
5	4:1	110	0.0	56.8	
6*	4:1	90	0.0	58.3	
7	6:1	120	0.0	42.0	Phenyl
8	1:4	100	81.2	5.6	
9	1:2	95	75.4	8.4	
10*	1:1	70	55.1	15.8	
11	4:1	97	13.7	67.0	Butyl
12**	6:1	70	—	45.4	
13					
14	1:4	75	78.6	1.2	
15	1:2	90	84.2	2.2	
16	1:1	124	72.3	4.2	
17*	4:1	65	8.0	53.3	
18*	6:1	65	2.4	63.5	Ethyl

* The experiment was carried out in a sealed tube.

** The polymeric product was formed in a sealed tube and was isolated by reprecipitation without first distilling off the liquid products.

Reaction of Phenyl Vinyl Ether with Carbon Tetrachloride at an Initial Ratio of 1 : 4

Preparation of Phenyl 1,3,3,3-Tetrachloropropyl Ether (II). A mixture of 61.4 g (0.4 mole) of carbon tetrachloride, 12 g (0.1 mole) of phenyl vinyl ether, and 1.1 g (0.0045 mole) of benzoyl peroxide was prepared in a two-necked flask fitted with stirrer and thermometer. The mixture was heated with stirring to 70-75°, at which temperature reaction usually set in and continued for two hours. Excess of carbon tetrachloride was distilled off, and vacuum distillation then gave a fraction, amounting to 26.2 g, of b.p. 145 - 145.5°, and 1.5 of polymeric residue. The constants of the fraction collected were b.p. 145-145.5° (9 mm); n_D^{20} 1.5432; d_4^{20} 1.3976; found MR 61.82; calculated for $C_9H_9OCl_3$ MR 61.27.

Found %: C 39.49; 39.61; H 3.10; 2.94; Cl 50.95; 51.08. $C_9H_9OCl_4$. Calculated %: C 39.45; H 2.94; Cl 51.76.

Found: M 252.1; 258.0. $C_9H_9OCl_4$. Calculated: M 273.98.

The product, which was obtained in 95.3% yield, was phenyl 1,3,3,3-tetrachloropropyl ether.

The results of the experiments on the reaction of phenyl vinyl ether with carbon tetrachloride in other proportions are given in Table 1.

Isolation and Characterization of the Polymeric Residue. After removal of unchanged phenyl vinyl ether and of phenyl tetrachloropropyl ether by distillation, there remained a clear orange viscous residue, which could not be distilled at 3 mm. When the residue was heated to 125°, it decomposed with evolution of hydrogen chloride and formation of a resinous substance. The residue was treated with steam until all traces of phenol, phenyl vinyl ether, and hydrogen chloride were gone, and it was then dried and analyzed.

Found %: C 62.45; 62.23; H 4.54; 4.49; C 23.33; 23.26. $C_{39}H_{32}O_4Cl_4$. Calculated %: C 62.54; H 5.09; Cl 22.37.

Found: M 619.3; 628.0. Calculated: M 634.4.

The residue was soluble in ether, methanol, and benzene, but it was insoluble in gasoline.

Reaction of Butyl Vinyl Ether with Carbon Tetrachloride in Presence of Benzoyl Peroxide

A series of experiments on reaction between butyl vinyl ether and carbon tetrachloride was carried out under the above-described conditions (or in sealed tubes heated to 70°) (see Table 1). Depending on the composition of the original mixture of reactants, various yields of the butyl tetrachloropropyl ether and the polymeric residue were obtained. Constants of the butyl tetrachloropropyl ether isolated were: b.p. 96.5 – 98.5° (6 mm); n_D^{20} 1.4695; d_D^{20} 1.2585; found MR 56.26; calculated for $C_7H_{12}OCl_4$, MR 55.64. The literature [7] gives: b.p. 51 – 52° (0.23 mm); n_D^{20} 1.4706; d_D^{20} 1.2610 [7].

The residue remaining after the removal of the butyl tetrachloropropyl ether was a clear viscous light-yellow polymeric product, soluble in ether and other organic solvents, other than methanol. It was purified by two reprecipitations with methanol from ethereal solution, and was dried in a desiccator at 35° and 20 mm.

The colorless viscous polymer had the following composition:

Found %: C 69.68; 69.54; H 11.68; 11.68; Cl 3.35; 3.22. For (I) when n=40 calculated %: C 69.63; H 11.64; Cl 3.32.

Reaction of Ethyl Vinyl Ether with Carbon Tetrachloride

The reaction of ethyl vinyl ether with carbon tetrachloride (in a flask or in sealed tubes) was studied under the same conditions. Ethyl 1,3,3,3-tetrachloropropyl ether and a polymeric residue were obtained (see Table 1). The constants of the ethyl tetrachloropropyl ether were: b.p. 72.5° (8mm); n_D^{20} 1.4700; d_4^{20} 1.3472; found MR 46.79; calculated MR 46.40. The literature [7] gives: b.p. 79–80° (11 mm); n_D^{20} 1.4695 [7].

Found %: C 26.29; 26.29; H 3.43; 3.41. $C_5H_8OCl_4$. Calculated %: C 26.58; H 3.57.

Found: M 212.0; 217.5. Calculated: M 225.94.

The residue was a clear viscous light-yellow substance of molecular weight 890.2; 897.1 (crude product!). As it was soluble in all organic solvents, it did not appear possible to purify it by reprecipitation.

Hydrolysis of Phenyl 1,3,3,3-Tetrachloropropyl Ether

Determination of Hydrogen Chloride in the Hydrolyzate. A mixture of 0.2347 g of the ether and 25 ml of distilled water was sealed in a tube, which was heated in a boiling water bath for one hour with periodic shaking. The contents of the tube were then transferred quantitatively to a 200 ml measuring flask. For the titration of 25 ml of the hydrolyzate, 2.35 ml of 0.0909 N NaOH was used, which corresponds to 0.0623 g of HCl or 1.99 moles of HCl per mole of the ether. The relation between the amount of HCl liberated and the hydrolysis conditions is shown in Table 2.

TABLE 2

No..	Hydrolysis conditions	Duration of hydrolysis	Temperature of hydrolysis (°C)	HCl (moles per mole of ether)	Notes
1	Shaking with water	1 min.	Room	0.01	
2	Shaking with water	1 hr.	Room	0.10	
3	Heating in sealed tube with water	30 min.	60	0.21	
4	Boiling under reflux with water	1 hr	100	1.86	
5	Heating in sealed tube with water	1 hr.	97	1.99	
6	Shaking with alkali	1 hr	Room	0.32	
7	Boiling with alkali	1 hr	100	2.25	Formation of resin
8	Boiling with alkali	1 hr	100	2.90	
9	Heating in sealed tube with alkali	1 hr	97	2.68	Slight explosion

Determination of Phenol in the Hydrolyzate. A mixture of 0.1954 g of the phenyl tetrachloropropyl ether and 25 ml of water was heated in a sealed tube in a boiling water bath for one hour. The contents of the tube were then transferred quantitatively to an Erlenmeyer flask, and bromine water was added with shaking until

precipitation of tribromophenol was complete. The precipitate was filtered off through a weighed glass filter, and it was washed with water (300 ml) until reaction for bromine was negative. The filter with the precipitate was dried to constant weight in a vacuum desiccator. The amount of tribromophenol obtained was 0.2075 g — or 0.2425 g (100.8% of the theoretical value) when allowance was made for dissolution by wash waters (solubility 0.04 g in 100 g of water at 15°). Similarly, from 0.2562 g of phenyl 1,3,3,3-tetrachloropropyl ether, 0.3101 g (98.7%) of tribromophenol was obtained.

Preparation of the Semicarbazone of 3,3-Dichloroacrolein. A mixture of 10.5 g of the phenyl tetrachloropropyl ether and 250 ml of water was prepared in a Favorsky flask attached to a condenser set for distillation. In the course of boiling for two hours a two-layer distillate slowly collected. The upper, aqueous layer of the distillate, and also the aqueous residue in the distillation flask, gave positive reactions for chlorine and phenol. The lower layer of the distillate — an oily liquid — was separated and was found to be 3,3-dichloroacrolein. Equimolecular amounts of semicarbazide and sodium acetate were dissolved in a few milliliters of ethanol. The solution was boiled for ten minutes, filtered, and added to a warm alcoholic solution of the dichloroacrolein. The precipitate of the semicarbazone which then formed was filtered off, recrystallized from boiling ethanol, and dried in a vacuum desiccator; m.p. 164.5-165° (in a sealed capillary).

Found %: N 23.67; 23.52. $C_4H_5N_3Cl_2O$. Calculated %: N 23.10.

Hydrolysis of Ethyl 1,3,3,3-Tetrachloropropyl Ether

A mixture of 0.1185 g of the ether and 25 ml of water was heated in a sealed tube in a boiling water bath for 30 minutes, and the hydrolyzate was then transferred quantitatively to an Erlenmeyer flask and titrated. The amount of 0.0909 N NaOH required was 11.2 ml, which corresponds to 0.0371 g of hydrogen chloride or 1.95 moles of HCl per mole of the ether. A parallel experiment gave 1.94 moles of HCl. The dichloroacrolein was isolated from the hydrolyzate as its semicarbazone, m.p. 164°, undepressed by admixture of an analytically pure specimen.

Reaction of Ethyl 1,3,3,3-Tetrachloropropyl Ether with Ethanol

At 35°, 5.4 g (0.12 mole) of ethanol was added dropwise with good stirring to a solution of 13.1 g (0.06 mole) of the ethyl tetrachloropropyl ether in 6 ml of carbon tetrachloride. The reflux condenser was provided with a trap containing distilled water for the absorption of hydrogen chloride. Cooling was applied in order to maintain the temperature of the reaction mixture at about 35°. When the alcohol had been added, the mixture was stirred for one hour at 60-65°. Fractionation gave 11.7 g (90%) of the diethyl acetal of 3,3,3-trichloropropionaldehyde, which had the following constants: b.p. 80 — 81° (9 mm); n_D^{20} 1.4450; d_4^{20} 1.1836; found MR 53.00; calculated for $C_7H_{13}O_2Cl_3$ MR 52.41. The literature [7] gives: n_D^{25} 1.4454; d_4^{20} 1.1829.

In the titration of the contents of the trap, 47.5 ml 1 N NaOH was required, which corresponds to 90.4% of the amount of HCl theoretically required by Equation 6.

Hydrolysis of the Diethyl Acetal of 3,3,3-Trichloropropionaldehyde (Equation 6)

A mixture of 1.6 g of the acetal and 5 ml of 2% HCl was refluxed for one hour. The hydrolyzate was cooled, and treatment with semicarbazide gave 1.0 g (83.4%) of a precipitate of the semicarbazone of 3,3-dichloroacrolein, m.p. 165.0° in a sealed capillary.

Found %: N 23.31; 23.35. $C_4H_5Cl_2ON$. Calculated %: N 23.10.

SUMMARY

1. A study was made of the conditions under which carbon tetrachloride reacts with phenyl vinyl, butyl vinyl, and ethyl vinyl ethers in presence of benzoyl peroxide.

2. It was found that, in presence of benzoyl peroxide, vinyl ethers are able to react with carbon tetrachloride with formation of both equimolecular-addition products and polymeric products, depending on the original proportions of reactants.

3. The characteristics of the resulting phenyl, ethyl, and butyl 1,3,3,3-tetrachloropropyl ethers were determined. Their hydrolytic decomposition was studied, and it was shown that, in the case of the phenyl ether, it can provide a quantitative method for the determination of the concentration of the ether.

4. The mobility of α-chloro in the 1,3,3,3-tetrachloropropyl ethers was demonstrated in hydrolytic-scission reactions and in the exchange reaction with an alcohol.

5. The polymeric products formed by addition of carbon tetrachloride to phenyl vinyl, ethyl vinyl, and butyl vinyl ethers were isolated and characterized.

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OPTICAL INVESTIGATION OF THE Si–H BOND AND PECULIARITIES IN ITS CHEMICAL BEHAVIOR IN VARIOUS COMPOUNDS

M. I. Batuev, A. D. Petrov, V. A. Ponomarenko and A. D. Matveeva

1. Many organosilicon and hydrosilicon compounds containing the Si–H bond have now been prepared, and these have aroused interest both from the theoretical and the practical points of view. The chemical evidence shows that the reactivity of the Si–H bond is greatly dependent on the nature of the other groups and atoms attached to the silicon atom in the given compound. In hydrosilicons the Si–H and Si–Si bonds are notable for their instability, as compared with the C–H and C–C bonds in hydrocarbons. It is sufficient to point out that, until recently, it has been found possible to prepare only the first six homologs of the silane series – as far as hexasilane Si_6H_{14}. Whereas oxygen has only a very feeble action on paraffins at ordinary temperatures, all silanes are spontaneously inflammable or explosive when brought into contact with the air: silane itself (SiH_4) reacts explosively with oxygen with formation of silica even at the temperature of liquid air, i.e. in hydrosilicons the Si–H bond (as also the Si–Si bond) is extremely reactive toward oxygen – and also toward halogens, alkalis, etc. [1]. However, the replacement of even one of the hydrogens of SiH_4 by a hydrocarbon radical greatly reduces the reactivity of the Si–H bonds; these organosilicon compounds are no longer spontaneously inflammable in the air [2]. The extent to which the reactivity of the Si–H bonds is changed depends on the character of the substituent radical. Thus, in compounds of the type R_3SiH, with increase in the length of the radical the rate of reaction with sodium hydroxide diminishes [3]. The rate at which addition occurs between unsaturated compounds and Si–H bonds is also greatly dependent on the identity of the atoms and groups (other than hydrogen) attached to the silicon atom [4].

This sensitivity of Si–H bonds to the structure of the molecule is manifested also in the Raman spectra of compounds containing such bonds, as we have already noted [5]. It is of considerable interest to determine the nature of this sensitivity with the aid of an optical investigation of a series of compounds and a comparison of these and other data with the corresponding data for C–H, and also O–H and F–H, bonds.

2. In the following sense one may speak of the protonization or electronization of the hydrogen atom in X–H bonds (X=Si, C, O, N, F, etc.). As is well known, the hydrogen atom of the hydroxy group varies greatly in its physical and chemical properties according to the nature of the compound in which the group is present. In strong acids, considerable protonization of this hydrogen occurs, i.e. a freeing of it, as a proton, from the electron-orbital system of the hydroxyl bond. On the other hand, in strong bases – particularly in the ion OH^- – electronization of the hydrogen atom occurs, i.e. its deeper involvement, as a proton, in the electron-orbital system of the hydroxyl bond and its screening by this electronic system. Optical investigations by one of us have shown [6] that the greater the protonization of the hydrogen atom of the hydroxyl group, the lower the vibration frequency and bond energy and the greater the O–H distance; on the other hand, the greater the electronization of the hydrogen atom, the higher the vibration frequency and bond energy and the lower the interatomic distance characterizing the hydroxyl bond. The range over which these parameters of the hydroxyl group vary is very considerable, as can be seen from the table given below.

Depending on the nature of R in compounds R–OH, these parameters may assume only intermediate values between those cited, their values being in accordance with the variation in the chemical nature of the O–H bond – in the strongest acids they may lie beyond the values for oxalic acid. In view of the higher Gordy electronegativity of the oxygen atom (3.45) as compared with hydrogen (2.13), in the extreme positions the oxygen atom tends to preserve its electron envelope in the octet form, i.e. almost in the form $(R\dot{\ddot{O}}\dot{X})^-$ $[H^+$ or $R^+|(\dot{X}\,\dot{\ddot{O}}\,\dot{X}H)^-$, whereas

in intermediate positions it approaches one of these forms in some measure or other, but under normal conditions it never approaches the form $R\dot{\ddot{O}}^{+}\ |\dot{\ddot{x}}|^{-}$. For the formation of an octet, the oxygen atom must use two foreign electrons. The presence of free paired electrons in the outer envelope of the oxygen atom and the tendency of the hydrogen atom to undergo protonization determine the donor properties of the oxygen atom and the acceptor properties of the hydrogen atom (possibility of its participation in hydrogen bonds).

	Hydroxyl of crystalline oxalic acid (β-form)	OH^- ion	Range of variation
Vibration frequency (cm^{-1})	2500	4200	1700
Bond energy (kcal/ mole)	51	145	94
Interatomic distance (A)	1.147	0.906	0.241

The tendency of the hydrogen atom to undergo electronization and protonization is apparent also in its bonds with atoms other than oxygen, and it varies greatly according to the nature of these atoms. In the H–F bond we have extreme protonization of the hydrogen atom, for the fluorine atom is still more electronegative (3.95) than the oxygen atom (3.45); hydrofluoric is one of the strongest acids: the octet of the fluorine atom is completed with the aid of only one foreign electron and its proton is almost free, $(:\ddot{\underset{\cdot\cdot}{F}}\dot{x})^{-}\ |\ H^{+}$. However, whereas the hydrogen atom in various R–OH compounds may pass into states varying from powerful protonization to powerful electronization according to identity of R, owing to the univalency of fluorine there can be only one compound containing H–F link–hydrogen fluoride itself. The donor and acceptor properties of fluorine and hydrogen atoms arise by virtue of the same circumstances as those existing in the case of the oxygen and hydrogen atoms of the hydroxy group, but they are manifested to an even higher degree•.

A very different picture is found for C–H bonds. The difference in electronegatively between its component atoms is not as great as in F–H and O–H, although the electronegativity of the H atom (2.13) is still lower than that of the C atom (2.55). This levelling of electronegativities with a certain predominance of electronegativity on the C atom considerably narrows the range over which the parameters of the C–H bond vary due to protonization and electronization of its H atom: there are no strong acids containing an almost completely protonized hydrogen atom $(RC\dot{x})^{-}\ |\ H^{+}$ (R is the remainder of the molecule), and, similarly, there are no compounds approaching $R^{+}\ |\ (CH)^{-}$. This is to be related to the fact that the C atom, unlike O and F atoms, has no unpaired electrons in saturated compounds – four foreign electrons $(\dot{\underset{\cdot}{\overset{\cdot}{x}}}C\dot{x})$, participate in its octet, so that it is firmly linked with the rest of the molecule. Electronization of the H atom in C–H bonds occurs as a result of the further involvement of the H atom in the electron envelope of the C atom without formation of the $(CH)^{-}$ ion and without any tendency for its formation when the C–H interatomic distance is shortened. The narrower range of variation of the parameters of C–H bonds can be seen from a comparison of the above-cited data for O–H bonds with the following data for C–H bonds [7].

The table shows that the introduction of double and triple bonds does not greatly affect the range of variation of the parameters of the C–H bond, which indicates the relative stability of C–H bonds, particularly in saturated compounds.

• It should be noted that the protonization of the hydrogen atoms of O–H and F–H bonds is aided by the rapid increase in the repulsive forces when the atoms of these bonds are brought closer together: as a result, the electron envelope "creeps" from the hydrogen atom and is attracted to the oxygen atom without the proton. This contrasts with the C–H and Si–H bonds: the electronegativity of the carbon atom is only a little greater than that of the hydrogen atom, and the electronegativity of the silicon atom is even less than that of the hydrogen atom; this "creeping" of the electron envelope under the influence of other atoms in the molecule is therefore not bound to occur in such bonds in saturated compounds it is attracted together with the proton, all the more since the "reserves" of interatomic distance in these bonds (in contrast with H–O and F–H bonds) for such attractions are appreciable, i.e. the repulsive forces do not yet prevent the attraction of the proton [6].

	Vibration frequency (cm^{-1})	Bond energy (kcal/mole)	Interatomic distance (A)
In the CH radical	2824	80.0	1.120
In C_2H_6 (6 frequencies in the range)	2730 – 2960	88.4	1.098
In C_2H_4 (4 frequencies in the range)	2988 – 3107	106.0	1.076
In C_2H_2 (2 frequencies in the range)	3288 – 3372	121.0	1.060
Range of variation	464 – 548	41.0	0.060

The Si – H bond is qualitatively different from the F – H, O – H, and C – H bonds in that the electronegativity of the hydrogen atom (2.13) exceeds that of its partner, the silicon atom (1.8); it is as if the latter acquires some of the character of a metal. Consequently, we can no longer speak of the protonization of the hydrogen atom in Si – H bonds in the sense of the formation of compounds of the form $(RSi)^{-}H^{+}$ (R is the remainder of the molecule), but we can now speak of greater or less electronization of the hydrogen atom in the Si – H bond. The acceptor properties of the hydrogen atom are repressed in the Si – H bond, but they are present in the silicon atom on account of its possible sexavalency (it is here, probably, that one of the causes of the instability of – Si – Si – Si – bonds is to be found: the readiness with which coordinational interaction between silicon atoms and atmospheric oxygen occurs results in the breakdown of hydrosilicon chains). We shall now turn to the elucidation of the changes in the electronization of Si – H bonds in various compounds with the aid of optical investigations. Below, we give the Raman spectra of three of these compounds; the spectra were determined on a Soviet ISP-51 spectrograph with a central camera*.

1. $(C_2H_5)_3SiH$, $\Delta\nu$ (cm^{-1}): 123(2), 176(2), 300(4*), 309(2*), 327(2*), 405(o), 584(10b), 642(3*), 672(3*), 709(4**), 723(3**), 813(6), 971(9), 1021(8), 1233(8), 1314(0), 1380(0), 1416(8), 1463(9), 2098(10 b), 2639(1), 2681(0), 2734(3), 2871(10*), 2888(10*), 2908(9*), 2933(4*), 2955(6*)

2. $(CH_3)SiH_2CH_2Cl$, $\Delta\nu$ (cm^{-1}): 176(1), 244(6), 257(0), 489(4), 582(9), 610(6*), 622(6*), 690(9), 731(0*), 746(1*), 753(6*), 764(6*), 815(2), 871(2), 944(5), 960(0), 1107(3), 1180(2), 1257(3), 1378(4*), 1434(4*), 2156(10, band), 2909(7sh), 2938(6*sh), 2968(4**sh), 2983(4**sh)

3. $(C_2H_5)SiHCl_2$, $\Delta\nu$ (cm^{-1}): 177(5*) 188(5*), 226(0), 264(0), 296(4), 493(10b), 548(3*), 566(3*), 660(5), 708(4), 799(5*), 813(5*), 975 (3 db), 1019(3 db), 1073(0), 1093(0), 1236(4), 1405(3), 1463(4), 2204(9b), 2747(1), 2829(1), 2889(7), 2914(2*), 2938(4*), 2973(3**), 2986(1**), (the lines 177-296 are on the background of the wing of the Raleigh line)

Spectra of the C – C – C – Si – C – C – C and C – C – C – C – C – C – Si compounds necessary for comparison have been published by us previously [5].

Before the spectrum measurements all these compounds are redistilled twice through a 35 plate column, and measures were taken to prevent the ingress of moisture into the cell. The compounds had the following boiling points: $(C_2H_5)_3SiH$ – 108.4° at 764.5 mm; $(CH_3)SiH_2CH_2Cl$ – 60° at 745.7 mm; $(C_2H_5)SiHCl_2$ – 74° at 744 mm.

3. We must first of all note the lower degree of interdependence between the vibrations of Si – H bonds when these are accumulated at a silicon atom, as compared with the vibrations of C – H bonds when these are accumulated at a carbon atom. For C – H bonds this interdependence is manifested in the splitting of their vibrations into a symmetrical and an antisymmetrical vibration in the CH_2 and CH_3 groups – and also in the raising of the vibration.

* Intensities are given on a ten-grade scale. The abbreviations used are b – broad line; sh – sharp line; db – double line; the asterisks indicate lines occurring on a background that is common with neighboring lines indicated by the same number of asterisks.

frequencies of C – H bonds as we pass from the methylidyne group, through the methylene and methyl groups, to methane, which is due to the ever increasing interaction of C – H bonds accumulating on a given carbon atom (the electron orbital of one hydrogen atom falls within the field of action of the nucleus of a second hydrogen atom and the electron orbital of the second hydrogen atom falls within the field of action of the nucleus of the first hydrogen atom with a resultant raising of the frequency of the antisymmetrical vibration and a less marked raising - in fact in some bonds, e.g. C – Cl, a lowering - of the frequency of the symmetrical vibration). There is a shortening of the C – H bonds, increase in their energy, etc. (and in the case of C – Cl bonds, lengthening, lowering of energy, etc.)*

In the case of Si – H bonds, their interaction when accumulated at a single silicon atom is not absent altogether, but is weak. The fact that interaction does actually occur is shown in the increase in Si – H vibration frequency as we pass from the SiH group, through SiH_2 and SiH_3, to SiH_4, and the feebleness of this interaction is shown by the fact that splitting of the vibration frequency of an Si – H bond into symmetrical and antisymmetrical vibration frequencies does not occur, only a rather considerable broadening of the Si – H line being observed. It is possible that a spectrograph having a considerably higher resolving power than ISP-51 would reveal the splitting of these frequencies, which is masked in our spectra by the broadening of the Si – H line.

TABLE

Increase in the Vibration Frequencies of C – H and Si – H Bonds in passing from the CH and SiH Groups to the CH_4 and SiH_4 Molecules

C – H bond			Si – H bond		
Compounds	Group	Frequency (cm^{-1})	Compounds	Group	Frequency (cm^{-1})
1. C – H bond	CH	2824	$(C_2H_5)_3$ SiH	SiH	2098
2. Normal paraffins	CH_2	2853s 2909a	C – C – C – Si – C – C – C	SiH_2	2127
3. Normal paraffins	CH_3	2879s 2967a	C – C – C – C – C – C – Si	SiH_3	2152
4. CH_4	CH_4	2915s 3072a	SiH_4 (liquid) [11]	SiH_4	2175
Rise from 1 to 4:		91 – 248	Rise from 1 to 4:		77

The increase in the vibration frequencies of C – H and Si – H bonds as we pass from the first compounds to the fourth is necessarily accompanied by increase in bond energy and decrease in interatomic distance, i.e. by the increased involvement of the nucleus of the hydrogen atom (the proton) in the electron-orbital system of the carbon and silicon atoms – electronization of the H atom of the C–H and Si–H bonds. The increase of electronization in this series of compounds is associated mainly with the interaction of bonds that we have discussed.

A substantial change in molecular structure (introduction of substituents having powerful effects, etc.) may produce the same effect as, or an even greater effect than, the interaction of bonds. Thus, replacement of a hydrogen atom by chlorine in the close vicinity of a silicon atom results in further increase in the electronization of the Si – H bond** - in an increase in frequency and bond energy, and in a reduction in interatomic distance, as will be seen from examples for SiH and SiH_2 groups:

Frequency SiH in $(C_2H_5)_3SiH$	2098 cm^{-1}
Frequency SiH in $(C_2H_5)Cl_2SiH$	2204 cm^{-1}
Increase	+106 cm^{-1}

* The accumulation of identical bonds on one atom results in a reduction in the dipole moment of the molecule, as shown in the work of Smyth and others [8] on the chloroalkanes; this reduction is related to changes in valency angles (mutual repulsion of chlorines), to the mutual induction of the dipoles of neighboring bonds (also called the vicinal effect [9]), etc. However, the dipole aspect of the interaction of these bonds, which would appear to result only in the strengthening of them [9], does not reveal the whole complexity of nucleus-electron interaction manifested, in particular, by the existence of antisymmetrical and symmetrical vibrations, which indicates an extension of the range of the possible physical states of these bonds and of their reactivity (cf., for example, an analogous phenomenon [10], which is shown in the chloroalkanes not only by the strengthening of the C–H bonds in CH_2 and CH_3, but also in their weakening, and not only by increase in their frequencies and energies, but also in decrease in these parameters; we shall not consider this in detail in the present paper).

** But not in its protonization, as is often stated for the C – H bond.

Frequency SiH in $C-C-C-Si-C-C-C$	2127 cm^{-1}
Frequency SiH in $CH_3-SiH_2-CH_2Cl$	2156 cm^{-1}
Increase	+29 cm^{-1}

The frequency of the Si – H bond in $(C_2H_5)Cl_2SiH$ is not only much greater than that in $(C_2H_5)_3SiH$, but is greater also than the Si – H frequencies in the SiH_2 and SiH_3 groups of the other compounds given above and in SiH_4. These data also show that the accumulation of chlorine atoms in the immediate vicinity of a silicon atom results in increase in the vibration frequency of the Si – H bonds, and therefore in an increase in bond energy and decrease in interatomic distance, i.e., it leads to their electronization.

Hence, variation in the reactivity of Si – H bonds in various compounds is to a great extent determined by the changes in the extent of the electronization of these bonds; in particular, its high value in SiH_4, together with the tendency of the silicon atom to enter into a coordination linkage with oxygen (discussed above), results in the high reactivity of this compound, which was discussed at the beginning of the paper.

The increase in the reactivity of the Si – H bond due to increase in its electronization under the influence of the accumulation of chlorine atoms in the close vicinity of the silicon atom, and also the polarization of the silicon atom itself brought about by this effect, is evidently manifested in the considerable increase in the yield of products of addition of R_3SiH to C=C–C–C–C in the following series of compounds: $(C_2H_5)_3CH_3SiH$ (very low yield), $(CH_3)Cl_2SiH$ (10% yield), Cl_3SiH (44% yield) [4]. The vibration frequency of the Si – H bond in Cl_3SiH is 2257 cm^{-1} [7], i.e., owing to its greater electronization in this compound, its frequency is higher than in $(C_2H_5)Cl_2SiH$, and in $(CH_3)Cl_2SiH$, in which there are only two chlorine atoms in the vicinity of the silicon atom (see above).

M. F. Zulina took part in the optical part of the experimental work, and L.L. Mkhitaryan helped in the preparation of the substance required in the investigation.

SUMMARY

1. Unlike O – H and F – H bonds, under normal conditions Si – H bonds cannot be described as protonized - only as more or less electronized.

2. In every concrete case, a change in the electronization of an Si – H bond that affects its chemical behavior must be considered in conjunction with other factors concerned with the structure of the reactant molecules and the reaction conditions.

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THERMAL TRANSFORMATIONS OF PIPERYLENE AT VARIOUS PRESSURES

N. I. Shuikin and T. I. Naryshkina

Study of thermal transformations of diene hydrocarbons is of interest not only from the theoretical, but also from the practical point of view. In some petroleum treatments lower conjugated dienes are formed, and knowledge of their behavior under the conditions of thermal treatment may result in improved control of the technological process.

Inadequate attention has been paid to investigation of the transformations of alkadienes. The literature shows that, in presence of various catalysts, diene hydrocarbons undergo dimerization, aromatization, hydrogenation, and polymerization reactions [1-4]. By the thermal treatment of piperylene at 600°, Frank and coworkers [5] obtained, apart from unchanged piperylene, only a light fraction, b.p. 38–41°, in 5% yield.

It was of interest to study the transformations of the diene piperylene at various pressures under high-temperature conditions. We have previously investigated the thermal transformations of piperylene at ordinary pressure [6]. In the present investigation we studied the thermal transformations of piperylene at 450-550°, both at a pressure of 20 mm, and also under 15 atm pressure of nitrogen. Pieces of quartz were used as filler. The experiments showed that changes in pressure and temperature have substantial effects on the transformations of piperylene. With increase in pressure from 20 mm to 15 atm at 550°, the amount of unchanged piperylene is lowered from 83.6% to 6.5%. At elevated pressure piperylene gives aromatic fractions consisting mainly of C_8–C_{10} hydrocarbons, whereas at ordinary pressure the aromatic fractions consist mainly of benzene, toluene, and xylenes. Rise in temperature from 450° to 550° increases the degree of conversion of piperylene; the yield of aromatic and resinous products increases, whereas that of low-boiling hydrocarbons, including unchanged piperylene, falls appreciably. With rise in temperature there is a considerable rise in the proportion of unsaturated hydrocarbons in the gaseous products.

EXPERIMENTAL

Transformations of Piperylene Under 15 atm Pressure of Nitrogen. The piperylene taken for investigation had the following properties: b.p. 42–43° (760mm); n_D^{20} 1.4315; d_4^{20} 0.6830. The literature [7] gives: b.p. 42.4–42.6°; n_D^{20} 0.4309; d_4^{20} 0.6803. The experiments were carried out in a flow-type apparatus, consisting of a feeding device (a "dropper"), a reaction zone filled with broken quartz, and a receiver. In each experiment 150 ml of piperylene was taken and was fed into the reaction zone at a rate of 0.3 hour^{-1}. The experiments were carried out at 450°, 500°, and 550° under a pressure of 15 atm. The compositions of some of the fractions were investigated with the aid of the Raman spectra*. In order to simplify the identification of the hydrocarbons present, some of the fractions were hydrogenated by Lebedev's method [8] and then subjected to adsorptional separation into paraffin–naphthene and aromatic parts—and also to distillation. The cyclopentadiene content of the condensate was determined by Afanasyev's method [9]. The gaseous products were analyzed in an Orsat and Lunge apparatus.

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* The spectrum analysis was carried out by Yu. P. Egorov, to whom we wish to express our thanks.

TABLE 1

Results of Experiments on the Thermal Transformations of Piperylene at 450°, 500°, and 550°

Temperature (°C)	Yield of condensate (%)	n_D^{20} of condensate	Composition of gas		
			H_2	C_nH_{2n}	C_nH_{2n+2}
450	74	1.4920	18.0	25.0	57.0
500	65	1.4980	20.4	35.0	44.6
550	59	1.5010	26.0	43.0	31.0

Results of typical experiments on the thermal treatment of piperylene at 450°, 500°, and 550° under a nitrogen pressure of 15 atm are presented in Table 1.

The liquid condensates were fractionated through a 30 plate column. All subsequent fractionations were carried out through the same column. The fractional composition and the properties of the fractions are given in Table 2. The fractionation curve of the condensate obtained in Experiment 1 at 450° is presented in Fig. 1. In the fractionation of the condensates, fractions boiling over the same range and having identical properties were obtained, and for the further analysis they were combined.

Investigation of the Fractions. Spectrum analysis of Fraction I and the physicochemical properties of this fraction (Table 2) showed that it consisted predominantly of 1-pentene, but contained also some 2-methyl-1-butene. It was shown that 1,4-pentadiene was also present, this being proved by its conversion into 1,2,4,5-tetrabromopentane, b.p. 162-165° (12 mm) and m.p. 85° [10].

Found %: C 15.63; H 2.21; Br 82.60. $C_5H_8Br_4$. Calculated %: C 15.49; H 2.08; Br 82.43.

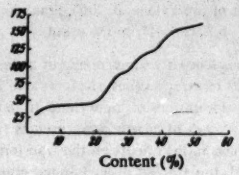


Fig. 1. Fractionation curve for the condensate from the thermal treatment of piperylene at 450°.

In the combined Fractions II and III, 2-methyl-1-butene (main component), trans-2-pentene, isoprene, and cyclopentadiene were detected by spectrum analysis. Fraction IV contained trans-piperylene. Fraction V consisted of a mixture of equal amounts of piperylene (cis and trans) and cyclopentadiene*.

The properties of the subsequent fractions showed that they contained a considerable amount of aromatic hydrocarbons in admixture with unsaturated hydrocarbons. Fractions VI, VIII, IX, and X, therefore, were hydrogenated in presence of platinum black [8]. The resulting mixtures of hydrocarbons did not contain any unsaturated compounds.

The hydrogenation results are given in Table 3.

Fraction VII was treated with 82% sulfuric acid, washed with sodium hydroxide solution and with water, and dried over calcium chloride. After being distilled over sodium it had n_D^{20} 1.4990 and b.p. 79-81° (750mm). This fraction, therefore, contained benzene.

After being hydrogenated, Fractions VI, VIII, IX, and X were combined and subjected to chromatographic separation. From 41 g of this mixture, 16 g of paraffins and naphthenes and 22 g of aromatic hydrocarbons were obtained. These were separated by precise fractional distillation and were identified by their physicochemical properties, their Raman spectra, and the results of Ullmann oxidation [11]. The analytical results for the paraffin–naphthene and aromatic parts are given in Tables 4 and 5. The fractionation was carried out in admixture with a decahydronaphthalene carrier.

An examination of the properties of the individual fractions given in Table 4 suggests that the fractions boiling in the range 36-68° contained pentane, 2,3-dimethylbutane, 2-methylpentane, and hexane. Spectroscopic data and the physicochemical properties indicate that the fractions boiling in the range 68-149° contained mainly cyclohexane homologs: methylcyclohexane, ethylcyclohexane, 1,3-dimethylcyclohexane, and 1-ethyl-3-methylcyclohexane.

* Determination of cyclopentadiene in the light part of the condensate (b.p. 26-160°) showed that in all the condensates it was present in a concentration of not more than 2%.

TABLE 2

Properties of Fractions of Condensates Obtained by Thermal Treatment of Piperylene at 450-550° under a Pressure of 15 atm

Fraction	Boiling range (corrected) (°C)	Experiment 1, 450°	Experiment 2, 500°	Experiment 3, 550°	Properties of combined fractions		Hydrocarbons detected spectroscopically
		Yield of fraction (% on condensate)			n_D^{20}	d_4^{20}	
I	26–32	4.0	3.2	1.8	1.3795	0.6540	1-Pentene (mainly), 2-methyl-1-butene
II	32–37	2.0	1.7	1.0	1.3880	0.6617	trans-2-Pentene, 2-methyl-1-butene, isoprene, cyclopentadiene
III	37–41	4.6	3.5	1.8	1.4040	0.6799	
IV	41–42	7.5	3.7	3.3	1.4285	0.7830	trans-Piperylene
V	42–45	9.2	4.2	3.2	1.4322	0.6838	Cyclopentadiene and trans-piperylene in equal amounts
VI	45–75	8.6	8.1	3.1	1.4650	0.7450	Benzene (mainly), 2-hexene, 3-hexene
VII	75–98	6.8	5.3	4.5	1.4780	0.7596	
VIII	98–112	8.0	6.6	4.3	1.4790	0.8270	—
IX	112–125	4.5	3.5	2.7	1.4775	0.8536	m–and p–Xylenes (ratio 1 : 2) and cycloalkenes, the composition of which was established after hydrogenation into the corresponding cycloalkanes (see Table 4)
X	125–160	14.8	20.3	28.6	1.4835	0.8501	
Residue		25.0	36.9	40.7	1.5098	—	
Losses		5.0	3.0	5.0	—	—	

Saturated hydrocarbons were obtained as a result of the hydrogenation of Fractions VI, VIII, IX, and X; thus, taking the spectrum data into account, it may be supposed that, apart from aromatic hydrocarbons, the original fractions contained also alkenes and cycloalkenes.

TABLE 3

Results of the Hydrogenation of Fractions VI, VII, IX, and X

Fraction	Amount taken for hydrogenation (g)	n_D^{20} of original fraction	Amount of hydrogenation product obtained (g)	n_D^{20} of hydrogenation product	Content of aromatic hydrocarbons (%)	Amount of hydrogen required for hydrogenation (liters, S.T.P.)
VI	16.0	1.4650	15.0	1.4380	30	5.8
VII, IX	18.8	1.4780	17.5	1.4690	62	2.1
X	17.5	1.4835	16.5	1.4700	80	3.0

From an examination of the properties of the individual fractions given in Table 5 it will be seen that the fraction of b.p. 78-80° consisted of benzene (6.8%). The succeeding fractions were oxidized to carboxylic acids with potassium permanganate, the amounts taken for oxidation being 3.5 g of the 135-136° fraction, 4 g of the 136-144° fraction, and 3.5 g of the 144-165° fraction. The resulting acids were separated and identified by the melting points of the acids themselves, their anhydrides, or their dimethyl esters. Benzoic acid melted at 119-120°, phthalic anhydride at 103°, dimethyl isophthalate at 62-63°, and dimethyl terephthalate at 136-138°. Hemimellitic and trimellitic acids melted at 188-190° and 210-216° respectively. On the basis of our

calculations we found that the 135-136° fraction contained 35% of ethylbenzene, 41% of m-xylene, and 24% of p-xylene; the 136-144° fraction contained 9% of o-xylene and 91% of p-xylene; the 144-165° fraction contained 43% of propylbenzene, 25% of 1-ethyl-3-methylbenzene, 16% of 1-ethyl-4-methylbenzene, 8% of 1,2,3-trimethylbenzene, and 8% of 1,2,4-trimethylbenzene.

TABLE 4

Fractional Composition of the Paraffin–Naphthene Part of the Hydrogenation Product

Boiling range of fraction (°C)	Amount (%)	Properties of fraction		Hydrocarbons established spectroscopically
		n_D^{20}	d_4^{20}	
36–38	22.0	1.3585	0.6268	
38–56	3.1	1.3750	0.6670	
56–57	15.5	1.3752	—	
57–68	6.3	1.3760	0.6599	
68–91	1.8	1.3920	—	Methylcyclohexane, 1,3-dimethylcyclohexane
91–118	7.5	1.4229	—	
118–130	12.5	1.4270	0.7820	1,3-Dimethylcyclohexane, ethylcyclohexane
130–144	15.5	1.4340	0.7898	Ethylcyclohexane, 1-ethyl-3-methylcyclohexane
144–149	9.5	1.4350	0.7900	
Losses	6.3	—	—	

TABLE 5

Composition and Properties of Aromatic Hydrocarbons Isolated from the Hydrogenation Product

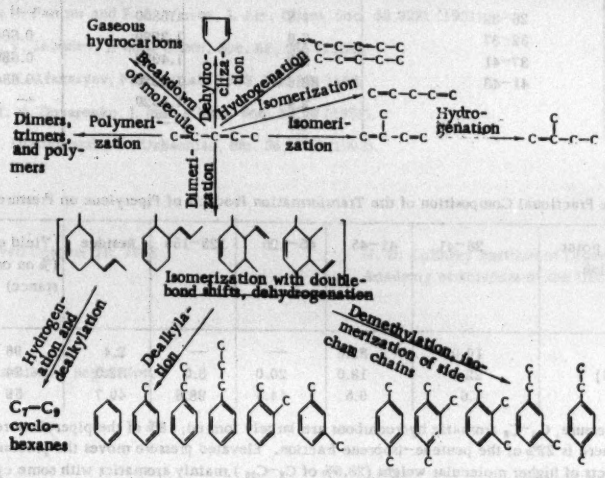
Boiling range of fraction (°C)	Amount (%)	Properties of fraction		MR		Hydrocarbons indicated by oxidation results
		n_D^{20}	d_4^{20}	Calculated	Found	
78–80	6.8	1.4990	0.8770	26.31	26.15	—
80–109	2.2	1.4980	—	—	—	—
109–110	6.8	1.4960	0.8665	30.93	31.06	—
110–135	2.7	1.4945	—	—	—	—
135–139	32.0	1.4940	0.8640	35.54	35.77	Ethylbenzene, m-xylene, p-xylene
139–144	24.0	1.4945	0.8600	35.54	35.97	p-Xylene, o-xylene
144–165	19.0	1.4937	0.8605	40.16	40.65	Propylbenzene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1,2,3- and 1,2,4-trimethylbenzenes
Losses	6.5					

All the residues collected in the fractionation of the condensates from all experiments were fractionated at reduced pressure (30 mm) and analyzed by oxidation and molecular weight determination. On the basis of the results it can be assumed that the residue contained not only the dimer, trimer, and tetramer of piperylene, but also C_{10} homologs of benzene and some naphthalene (m.p. 79°; picrate m.p. 148°).

Hence as a result of thermal transformations of piperylene under high-pressure conditions, hydrocarbons of various classes are formed: C_5–C_7 alkenes, cyclohexene homologs, benzene and its homologs, isomerization (isoprene) and dehydrocyclization (cyclopentadiene) products, and also piperylene dimers, trimer, and tetramers and naphthalene.

This great variety of products indicates that, under the selected conditions, the thermal transformations of piperylene are accompanied by synthetic processes. It must be supposed that aromatic hydrocarbons are formed by dehydrogenation and dealkylation of piperylene dimer, which is readily formed at high temperatures [4]. It may be supposed also that the original substance breaks down into radicals of varying degrees of complexity, including methylene radicals, and these effect the alkylation of piperylene or its transformation products.

The compositions of the products of the thermal treatment of piperylene at elevated pressure are represented in the following scheme:



Transformations of Piperylene at Reduced Pressure. In order to determine the effect of reduced pressure on the character of the transformations of piperylene, experiments were carried out in a flow-type apparatus. Passage of the hydrocarbon over the same broken quartz at 550° at a rate of 0.3 hour $^{-1}$ at 20mm gave a condensate having n_D^{20} 1.4310 in 96% yield. The cyclopentadiene content did not exceed 1.5%. Results of the fractionation of 50 g of the condensate through a column (see above) are given in Table 6.

Analogy with the results already obtained on the compositions of the fractions of the condensate obtained under high-pressure conditions and consideration of the resemblance of the properties of fractions boiling over the same temperature range indicated that the first three fractions (26-41°) contained 1,4-pentadiene, 1- and 2-pentenes, 2-methyl-1-butene, cyclopentadiene, and isoprene. All these hydrocarbons were actually found in these fractions when Raman spectrum analysis was carried out. In the residues that accumulated during the fractionation of the condensates, aromatic hydrocarbons (benzene, toluene) were found only in insignificant amounts.

Comparative Characterization of the Thermal Transformations of Piperylene at Different Pressures. Comparison of the results on the thermal transformations of piperylene at different pressures shows that pressure has a substantial effect on the composition of the product (Table 7). For comparison we take the results of experiments carried out at 550°.

An examination of these results shows that the degree of conversion of piperylene into liquid products at low pressure does not exceed 13% and 83.6% of the original piperylene remains unchanged. Under reduced-pressure conditions, side reactions are greatly depressed. In the experiments which were conducted

TABLE 6

Fractional Compositions of the Condensate Obtained by Thermal Treatment of Piperylene at 550° and 20 mm

Fraction	Boiling range (°C)	Yield of fraction (%)	Properties of fraction	
			n_D^{20}	d_4^{20}
I	26–32	1.8	1.3800	—
II	32–37	6.0	1.3990	0.6641
III	37–41	2.2	1.4058	0.6802
IV	41–43	83.6	1.4320	0.6840
Residue		2.4	1.4520	—
Losses		4.0	—	—

TABLE 7

Dependence of the Fractional Composition of the Transformation Products of Piperylene on Pressure (550°)

Pressure / Boiling point of fraction (°C)	26–41	41–45	45–125	125–160	Residue	Yield of condensate (% on original substance)
20 mm	10.0	83.6	—	—	2.4	96
Atmospheric [6]	22.0	18.0	20.0	8.0	32.0	74
15 atm	4.6	6.5	14.6	28.6	40.7	59

at atmospheric pressure, C_6–C_8 aromatic hydrocarbons are largely formed; 18% of the piperylene remains unchanged, and there is 22% of the pentene–isoprene fraction. Elevated pressure moves the process in the direction of products of higher molecular weight (28.6% of C_8–C_{10}), mainly aromatics with some cyclohexane hydrocarbons; only 6.5% of the piperylene remains unchanged and there is 4.6% of the pentene–isoprene fraction (26-41°). Moreover, a large amount of high-boiling hydrocarbons is formed: cyclicpolymerization and condensation products of piperylene.

SUMMARY

1. The thermal transformations of piperylene were investigated at 450-550° under elevated pressure in a flow system.

2. As a result of these transformations at elevated pressure, a complex mixture of hydrocarbons of various classes was formed: pentenes, hexenes, isoprene, cyclopentadiene, cyclohexene homologs, aromatic hydrocarbons, and products of the cyclic polymerization of piperylene.

3. The presence of these hydrocarbons in the condensates gives reason to suppose that, under the given conditions, isomerization, dehydrocyclization, hydrogenation, polymerization and dimerization, with subsequent dehydrogenation and dealkylation occur.

4. A comparison was made of the compositions of the products of the thermal treatment of piperylene at various pressures (15 atm, atmospheric, and 20 mm).

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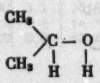
EFFECT OF THE METHOD OF PREPARATION AND THE PRESENCE OF A CARRIER ON THE CATALYTIC ACTIVITY OF CHROMIC OXIDE IN DEHYDROGENATION AND DEHYDRATION REACTIONS

A. A. Tolstopyatova, K. A. Dulitskaya, and A. A. Balandin

We are at present carrying out investigations on the determination by the kinetic method of the energies of the bonds between reacting molecules and catalysts. Such data may be applied in the development of the theory underlying the selection of catalysts [1]. We decided to investigate the behavior of chromic oxide in the reactions of dehydrogenation of methylcyclohexane, dehydrogenation and dehydration of isopropyl alcohol [2], and dehydrogenation of formic acid. The object of the present investigation was to determine the effects of the following factors on reaction rate, activation energy, and bond energy: 1) the identity of the precipitant used in the preparation of chromic oxide; 2) the presence of asbestos as carrier; 3) the nature of substituents on atoms that participate directly in the reaction (substituents not in sphere of reaction). The existence of such effects can be explained theoretically by the influence of the number and the nature of neighboring atoms on the reacting atoms in the intermediate catalytic complex at an active center.

We have previously studied chromic oxide prepared by precipitation of chromic nitrate with sodium carbonate and subsequent decomposition of the resulting hydroxide into oxide [2]. In order to determine the effect of the identity of the precipitant used in the preparation of the catalyst, in the present investigation chromic oxide was prepared by the same method as before [2], but instead of sodium carbonate, ammonia was used as precipitant (Catalyst No. 1). In order to determine the effect of the presence of a carrier, chromic hydroxide prepared as before [2] was formed on asbestos, the hydroxide then being decomposed into oxide (Catalyst No. 2).

In order to determine the effect of the nature of substituents on atoms that participate directly in the reaction, a comparison may be made between the dehydrogenation of isopropyl alcohol and that of formic acid, for which the indices are identical, i.e. identical atoms participate directly in the reaction, but the substituents are different:



Dehydrogenation of isopropyl alcohol

Dehydrogenation of formic acid

EXPERIMENTAL

Preparation of Catalysts

Catalyst No.1. A 10% solution of chromic nitrate [$Cr(NO_3)_3 \cdot 9H_2O$, pure] was prepared at 80°, 20% ammonia was stirred in, and stirring was continued until precipitation was complete. The precipitate was washed by decantation until reaction of nitrate (with diphenylamine) was negative. The precipite was then filtered off and dried in a drying cupboard at 110 - 120°. A portion of the catalyst was then placed in a catalysis tube and heated in a current of air in an electric furnace with gradual raising of temperature until water ceased to separate (350°).

Catalyst No. 2. Asbestos was impregnated with 10% chromic nitrate [$Cr(NO_3)_3 \cdot 9H_2O$ (pure)] and 10% sodium carbonate solution was added with stirring until precipitation was complete. Both solutions were first heated to 80°. The further treatment was the same as for the preparation of Catalyst No. 1. Proportions of asbestos and chromic oxide 1 : 1.

The asbestos was first purified in the usual way. Fibrous asbestos was placed in a porcelain dish and covered with concentrated sodium hydroxide solution. It was left for 24 hours, washed so as to remove most of the alkali, covered with a 9 : 1 mixture of nitric acid and hydrochloric acids, heated in a water bath for ten hours, washed until reaction for chlorine was negative, dried in a drying cupboard, and roasted in a muffle.

Starting Substances

Methylcyclohexane: b. p. 100.2° (760 mm); n_D^{20} 1.4230; d_4^{20} 0.7692. Isopropyl Alcohol, 96.0%: b. p. 81–82° (763.5 mm); d_4^{20} 0.8002. Formic Acid, 85%: d_4^{20} 1.1950.

Apparatus and Experimental Procedure

The experiments were carried out by the usual flow method. The reactor was a quartz tube, diameter 18 mm, length 90 cm. It was placed in an electric furnace. The temperature was measured within 0.5° with a chromel-alumel thermocouple connected to a potentiometer. The thermocouple pocket was placed in the center of the layer of catalyst. The starting substance was passed in from a medical glass syringe; the rate of feed was controlled by means of a Warren electric motor, and was 0.23 ml per minute for all of the substances.

Gas was collected in a eudiometer having a constant lower level and was analyzed in a VTI apparatus. During the experiments the volume of gas formed was measured accurately within 0.5 ml. Gas for analysis was collected 10-12 minutes after the establishment of a stationary state. The duration of an experiment was 30-40 minutes.

Dehydrogenation of Methylcyclohexane (Catalyst No. 1.)

In the dehydrogenation of methylcyclohexane in the temperature range 366-427°, analysis showed that the gaseous products contained 99% of hydrogen and not more than 1% of other gases. The reaction went in accordance with the equation $C_6H_{11}CH_3 - 3H_2 + C_6H_5CH_3$. The activation energy, calculated by the Arrhenious equation for the dependence of log m_{H_2} (m_{H_2} is the volume of hydrogen (ml at STP) formed per minute) on $1/T$, is found to be ϵ_{H_2} = 22,000 cal/mole. The points for the relation between log m and $1/T$ fit satisfactorily to a straight line (Fig. 1). The experimental results are shown in Table 1 and Fig. 1. As can be seen from Table 1, the reciprocal of the scatter parameter $\frac{\epsilon}{\log k_0} \cdot 10^{-3} = 2.6$; $\log k_0 = \log m_{H_2} + \frac{\epsilon}{4.57T}$.

TABLE 1

Dehydrogenation of Methylcyclohexane
(Catalyst No. 1, 7 g, 8-cm layer; rate of feed 0.23 ml/minute; ϵ_{H_2} = 22,000 cal/mole)

Experiment	Temperature of exper. (°C)	m_{H_2} (ml/min.)	Conversion (%)	log k_0	$\frac{\epsilon}{\log k_0} \cdot 10^{-3}$
7	366	7.8	6.4	8.42	2.61
10	366	7.5	6.2	8.40	2.61
3	384	12.9	10.6	8.43	2.61
8	406	22.4	18.4	8.44	2.60
4	407	22.4	18.4	8.59	2.56
5	427	40.0	32.9	8.47	2.59
9	417	29.4	24.2	8.44	2.60
			Mean		2.6

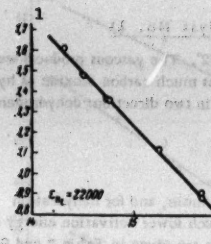
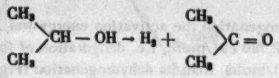


Fig. 1. Dehydrogenation of methylcyclohexane (Catalyst No. 1).

Dehydrogenation and Dehydration of Isopropyl Alcohol (Catalyst No. 1)

Over chromic oxide in the temperature range 280-340°, isopropyl alcohol undergoes two reactions simultaneously – dehydrogenation and dehydration. In the gas analysis, 70 -80 % of hydrogen and 20-30% of unsaturated hydrocarbons were found; the total amount of CO and CO_2 was less than 1%. The reactions occurring were:



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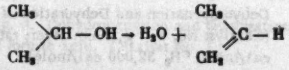


TABLE 2

Dehydrogenation and Dehydration of Isopropyl Alcohol (Catalyst No. 1, 7 g, 8-cm layer; rate of feed of alcohol 0.23 ml/minute)

Experiment	Temperature (°C)	m_{H_2O} (ml per min)	C_nH_{2n} (ml per min)	m_{H_2} (ml H_2 per min)	Composition of gas: C_nH_{2n} (%)	Composition of gas: H_2 (%)	Conversion into: C_nH_{2n} (%)	Conversion into: H_2 (%)	$\log k_{H_2}$	$\log k_{H_2}$	$\frac{\varepsilon_{H_2}}{\log k_{H_2}} \cdot 10^{-3}$	$\frac{\varepsilon_{H_2O}}{\log k_{H_2O}} \cdot 10^{-3}$	Activation energy (cal/mole)
9	280	2.0	7.1	22.1	76.9	2.92	10.32	5.82	5.74	2.4	2.2	ε_{H_2} = 12 350
8	300	3.3	12.3	21.1	77.9	4.78	17.90	5.84	5.81	2.4	2.1	ε_{H_2O}=13 950
5	319	4.6	14.2	24.5	74.5	6.70	20.64	5.82	5.71	2.4	2.2	
4	320	4.0	13.3	22.7	76.3	5.84	19.34	5.75	5.68	2.4	2.2	
6	331	6.8	17.0	28.7	70.3	9.97	24.71	5.82	5.64	2.4	2.2	
10	340	6.8	16.5	29.3	69.7	9.97	24.0	5.82	5.62	2.4	2.2	
12	280	2.0	7.0	22.0	78.0	2.90	10.30	6.40	5.51	2.4	2.14	ε_{H_2} = 11 800
11	291	3.2	7.2	30.8	68.2	4.70	10.40	6.41	5.44	2.4	2.17	ε_{H_2O}=15 200
13	313	5.1	11.3	30.9	68.1	7.37	16.23	6.38	5.45	2.4	2.16	
14	315	5.4	11.6	31.4	67.6	7.85	16.96	3.99	5.44	2.4	2.17	
15	331	7.2	14.3	33.1	65.9	11.25	22.40	66.3	5.43	2.4	2.17	
16	347	8.5	16.4	33.8	65.2	12.35	23.80	6.29	5.37	2.4	2.19	ε_{H_2} = 980
17	280	1.9	7.53	19.7	79.3	2.72	10.95	6.34	4.76	2.4	2.0	ε_{H_2O}=15 300
20	290	2.6	9.6	21.3	77.1	3.81	13.90	6.36	4.79	2.4	2.0	
18	300	3.1	10.4	22.6	76.4	4.47	15.10	6.33	4.76	2.4	2.0	
19	320	5.4	14.8	26.6	72.4	7.93	21.58	6.38	4.79	2.4	2.0	
21	330	6.0	15.4	27.9	71.1	8.80	22.43	6.33	4.75	2.4	2.0	

The experimental results are given in Table 2 and Fig. 2. As the amount of work done by the catalyst increased, the activation energy for the dehydrogenation reaction diminished; thus for the first ten experiments ε_{H_2} = 12,350 cal/mole, for the next five ε_{H_2} = 11,800 cal/mole, and for the next five ε_{H_2} = 9800 cal/mole. On the other hand, for the dehydration reaction the activation energy increased as the amount of work done by the catalyst increased, and it finally became constant. Thus, for the first ten experiments ε_{H_2O} = 13,950 cal/mole, for the next five ε_{H_2O} = 15,200 cal/mole, and the next five ε_{H_2O} = 15,300 cal/mole (Fig. 2). The value of $\frac{\varepsilon}{\log k_0} \cdot 10^{-3}$ for the dehydration of isopropyl alcohol had the mean value of 2.4, and for the dehydrogenation reaction it varied from 2.2 to 2.0.

Dehydrogenation and Dehydration of Formic Acid (Catalyst No. 1)

The decomposition of formic acid was carried out in the range 227-272°. The gaseous products were found to contain 12.6-32.0% of hydrogen, 37-74% of carbon monoxide, and as much carbon dioxide as hydrogen. This gives reason to suppose that the decomposition of formic acid proceeds in two direction–dehydrogenation and dehydration:

$$HCOOH \rightarrow CO_2 + H_2 \rightleftarrows HCOOH \rightarrow CO + H_2O.$$

For dehydrogenation the activation energy was found to be ϵ_{H_2} = 32,000 cal/mole, and for dehydration ϵ_{H_2O} = 12,700 cal/mole, i.e. dehydration of formic acid proceeds with a much lower activation energy (by 19,300 cal/mole), than its dehydrogenation (Fig.3). The experimental results are given in Table 3 and Fig. 3.

TABLE 3

Dehydrogenation and Dehydration of Formic Acid
(Catalyst No. 1, 7 g, 8-cm layer; rate of feed of acid 0.23 ml/minute; ϵ_{H_2O} 12,700 cal/mole, ϵ_{H_2} 32,000 cal/mole)

Experiment	Temperature (°C)	Total amount of gas in (ml/minute)	m_{H_2} (ml H_2 per min)	m_{CO} (ml CO per min)	Composition of gas		Conversion		$\log k_{H_2}$	$\log k_{CO}$	$\frac{\epsilon}{\log k} \cdot 10^{-3}$ H_2	$\frac{\epsilon}{\log k} \cdot 10^{-3}$ CO
					H_2 (%)	CO (%)	H_2 (%)	CO (%)				
1	227	8.7	1.1	6.4	12.6	74.3	0.80	4.71	14.03	6.36	2.3	2.0
2	243	16.9	3.0	10.9	18.0	65.2	2.25	8.08	14.04	6.42	2.3	2.0
5	244	16.8	3.2	10.4	19.5	62.8	2.40	7.70	14.04	6.38	2.3	2.0
3	261	30.6	7.9	14.7	26.4	49.0	5.94	10.92	14.01	6.37	2.3	2.0
4	272	48.9	15.5	17.8	32.0	36.9	11.60	13.22	14.04	6.34	2.3	2.0

Dehydrogenation of Methylcyclohexane (Catalyst No. 2, Cr_2O_3–asbestos)

The dehydrogenation of methylcyclohexane proceeded in the temperature range 470-540°. Only hydrogen was found in the gas. The activation energy for the dehydrogenation of methylcyclohexane is ϵ_{H_2} = 27,000 cal/mole. The points fit well to a straight line. The quantity $\frac{\epsilon}{\log K_\theta} \cdot 10^{-3} = 3.2$. On Catalyst No. 2 ($Cr_2O_3$–asbestos) this reaction proceeds less readily than on Catalyst No. 1; the difference in activation energies is 5000 cal/mole. The results of the experiments are given in Table 4 and Fig. 4.

Dehydrogenation and Dehydration of Isopropyl Alcohol (Catalyst No. 2, Cr_2O_3–asbestos)

The dehydrogenation and dehydration of isopropyl alcohol was carried out in the range of 340-400°. The gas contained 60-78% of hydrogen and 22-40% of unsaturated hydrocarbons. The other gases present did not amount to more than 1%. The activation energy for the dehydrogenation reaction was ϵ_{H_2} = 17,100 cal/mole and that for dehydration was ϵ_{H_2O} = 28,600 cal/mole. For Catalyst No. 2 the activation energies for dehydrogenation and dehydration were greater than for Catalyst No. 1. The results of the experiments are given in Table 5 and Fig. 5.

Dehydrogenation and Dehydration of Formic Acid (Catalyst No. 2, Cr_2O_3–asbestos)

The decomposition of formic acid over Catalyst No. 2 in the temperature range 244-283° proceeded by dehydration and dehydrogenation. In the gaseous products, carbon monoxide, carbon dioxide, and hydrogen were found, the amounts of carbon dioxide and hydrogen being identical. The activation energy for the dehydration reaction was ϵ_{H_2O} = 35,000 cal/mole, and that for the dehydrogenation reaction was ϵ_{H_2} = 14,200 cal/mole (Fig. 6). The experimental results are given in Table 6.

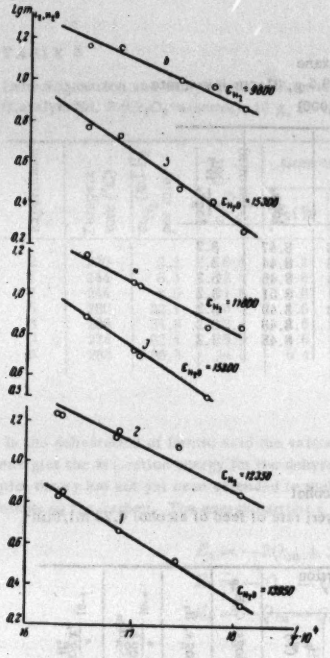


Fig. 2. Effect of catalyst activity on the dehydrogenation and dehydration of isopropyl alcohol: 1 and 2 —Experiments 5-10; 3 and 4 —Experiments 11-15; 5 and 6 —Experiments 16-21 (Table 2). Catalyst No. 1.

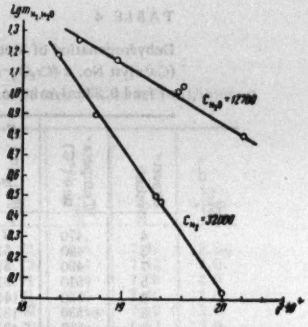


Fig. 3. Dehydrogenation and dehydration of formic acid. Catalyst No. 1.

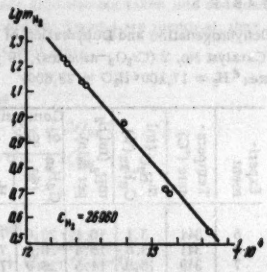


Fig. 4. Dehydrogenation of methylcyclohexane. Catalyst No. 2.

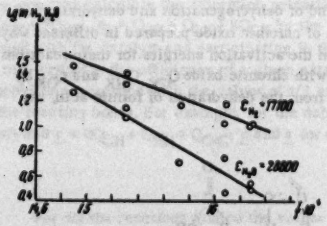


Fig. 5. Dehydrogenation and dehydration of isopropyl alcohol. Catalyst No. 2.

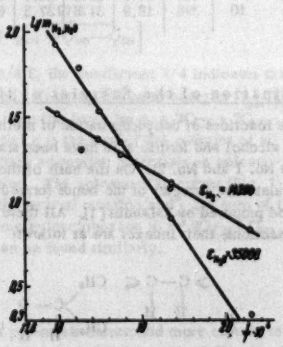


Fig. 6. Dehydrogenation and dehydration of formic acid. Catalyst No. 2.

TABLE 4

Dehydrogenation of Methylcyclohexane
(Catalyst No. 2 (Cr_2O_3–asbestos), 19.5 g, 31-cm layer; rate of feed 0.23 ml/minute; $\epsilon_{H_2} = 27{,}000$)

Experiment	Temperature (°C)	m_{H_2} (ml H_2 per min)	Conversion (%)	$\log k_1$	$\frac{\epsilon}{\log k_1} \cdot 10^{-3}$
4	470	3.6	2.95	8.47	3.2
3	490	5.1	4.23	8.44	3.2
7	490	5.3	4.36	8.46	3.2
5	510	9.5	7.81	8.51	3.2
6	530	14.0	11.53	8.49	3.2
8	530	13.8	11.37	8.48	3.2
9	540	17.0	14.0	8.48	3.2

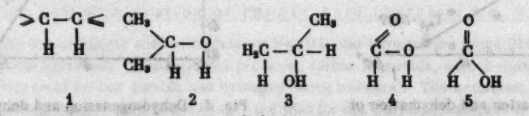
TABLE 5

Dehydrogenation and Dehydration of Isopropyl Alcohol
(Catalyst No. 2 (Cr_2O_3–asbestos), 10 g, 17-cm layer; rate of feed of alcohol 0.23 ml/minute; $\epsilon_{H_2} = 17{,}100$ $\epsilon_{H_2O} = 28{,}600$)

Experiment	Temperature (°C)	m_{H_2O} (ml C_nH_{2n} (%)	m_{H_2} (ml H_2 per min)	Composition of gas		Conversion into		$\log k_1$, C_nH_{2n}	$\log k_1$, H_2	$\frac{\epsilon}{\log k_1} \cdot 10^{-3}$	$\frac{\epsilon}{\log k_1} \cdot 10^{-3}$
				C_nH_{2n} (%)	H_2 (%)	C_nH_{2n} (%)	H_2 (%)				
5	341	3.1	10.4	23.0	77.0	4.48	15.02	10.68	7.11	2.7	2.4
8	341	3.6	10.4	26.0	74.0	5.25	15.02	10.75	7.11	2.6	2.4
7	349	5.6	14.5	28.0	72.0	8.13	20.94	10.81	7.18	2.6	2.4
12	349	2.9	10.8	21.4	78.6	4.23	15.60	10.53	7.05	2.7	2.4
11	363	5.2	15.0	25.9	74.1	7.56	21.66	10.56	7.06	2.7	2.4
4	380	11.9	25.7	31.8	68.2	17.26	37.11	10.66	7.14	2.7	2.4
9	380	14.3	25.2	36.1	63.9	20.45	36.10	10.74	7.13	2.7	2.4
10	398	18.9	31.6	37.2	62.8	27.10	45.60	10.60	7.07	2.7	2.4

Determination of the Energies of the Bonds Formed by C, H, and O with Cr_2O_3

The reactions of dehydrogenation of methylcyclohexane and of dehydrogenation and dehydration of isopropyl alcohol and formic acid have been studied in presence of chromic oxide prepared in different ways (Catalysts No. 1 and No. 2). On the basis of the data obtained on the activation energies for these reactions we may calculate the energies of the bonds formed by C, H, and O with chromic oxide Q_{CK}, Q_{HK} and Q_{OK} by the method proposed by Balandin [1]. All these reactions, apart from the dehydration of formic acid, are doublet reactions; their indexes are as follows:



1	2	3	4	5
Dehydrogenation $C_6H_{11}CH_3$	Dehydrogenation i-C_3H_7OH	Dehydration i-C_3H_7OH	Dehydrogenation HCOOH	Dehydration HCOOH

TABLE 6

Dehydrogenation and Dehydration of Formic Acid
(Catalyst No. 2 (Cr_2O_3–asbestos), 16 g, 23-cm layer; rate of feed of acid 0.23 ml/minute)

Experiment	Temperature (°C)	m_{H_2} (ml H_2 per min)	m_{CO} (ml CO per min)	Conversion		$\log k_{H_2}$	$\frac{1}{T}\cdot 10^3$	$\log k_{CO}$	$\frac{1}{T}\cdot 10^3$
				H_2 (%)	CO (%)				
2	220	2.1	6.8	0.2	5.0	14.77	2.4	7.12	2.0
1	244	8.1	12.8	0.6	9.4	14.72	2.4	7.12	2.0
7	244	8.0	11.8	0.6	8.7	14.71	2.4	7.08	2.0
5	260	22.1	19.2	1.6	14.2	14.71	2.4	7.10	2.0
8	268	34.8	23.4	2.6	17.8	14.69	2.4	7.10	2.0
3	274	62.1	19.9	4.6	14.8	14.79	2.4	6.97	2.0
6	283	86.3	34.0	6.4	25.2	14.70	2.4	7.11	2.0

In the dehydration of formic acid the valency of carbon changes, and therefore in the calculation of bond energies the activation energy for the dehydration of formic acid was not taken into consideration: the multiplet theory has not yet been extended to such reactions. Indices 2 and 4 are identical; they differ in the substituents on the carbon. The energy barriers E for these reactions are:

$$E_1 = -2Q_{CH} + 2Q_{CH} + 2Q_{HH}$$
$$E_2 = -Q_{CH} - Q_{OH} + Q_{CH} + Q_{OH} + 2Q_{HH}$$
$$E_3 = -Q_{CH} - Q_{CO} + Q_{HH} + Q_{OH} + 2Q_{CH}$$

Solving these equations, we may find Q_{HK} Q_{CK} and Q_{OK}:

$$Q_{HH} = \frac{1}{2}\left[\frac{1}{2}E_1 + (E_2 - E_3) + \overbrace{Q_{CH} + Q_{OH} - Q_{CO}}^{124.0}\right]$$

$$Q_{CH} = \frac{1}{2}\left[\frac{1}{2}E_1 + (E_3 - E_2) + \overbrace{Q_{CO} + Q_{OH} - Q_{CH}}^{57.0}\right]$$

$$Q_{OH} = \frac{1}{2}\left[(E_2 + E_3) - \frac{3}{2}E_1 + \overbrace{Q_{CO} + Q_{OH} - Q_{CH}}^{97.2}\right]$$

Knowing ϵ, we may calculate E from the formula $\epsilon = 3/4\ E$; the coefficient 3/4 indicates that the bonds may not be completely broken in the reaction, but only deformed. Knowing the bond energies Q_{CK}, Q_{HK}, and Q_{OK}, we may calculate the adsorption potentials q_1, q_2, and q_3 from the formulas $q_1 = 2Q_{CK} + 2Q_{HK}$; $q_2 = Q_{CK} + Q_{CK} + 2Q_{HK}$; $q_3 = Q_{HK} + Q_{OK} + 2Q_{CK}$ for the adsorption potential q is the sum of the energies of all the bonds formed with the catalyst and participating in the reaction. Plotting adsorption potentials on volcano-like curves, we may estimate the efficiency of a given catalyst in any reaction. The volcano-like curves (Fig. 7) are constructed in accordance with the values of $s/2$ and $u/2$, u being the heat of reaction and s the sum of the energies of the reacting bonds. For example, for the dehydrogenation of methylcyclohexane $u_1 = -2Q_{CH} + Q_{HH} + Q_{C=C}$ (second bond) and $s = 2Q_{CH} + Q_{HH} + Q_{C=C}$; u and s for other reactions can be found similarly.

For all the reactions studied the values of the adsorption potentials correspond more closely to the peaks of the volcano-like curves in the case of Catalyst No. 1 than in the case of Catalyst No. 2 (Fig. 7). This means that Catalyst No. 1 is more active than Catalyst No. 2, but is less capable of being improved. This conclusion

must follow from the fact that the nearer the intersect of the adsorption potential to the peaks of the volcano-like curves, the more active the catalyst; when the intersect passes through the maximum of the curve, the catalyst is of maximum activity for the given reaction. It should be noted also that the more active catalyst (No. 1) has a lower energy of activation than Catalyst No. 2.

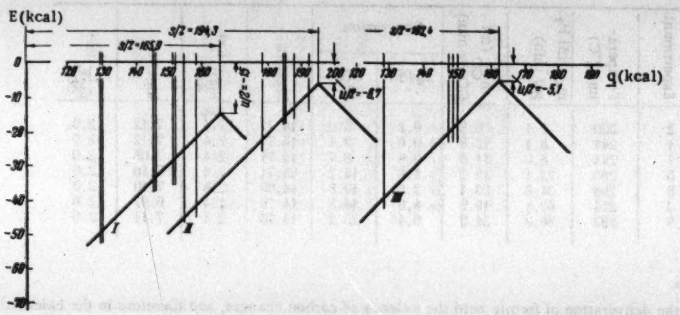


Fig. 7. Volcano-like curves: I—dehydrogenation of methylcyclohexane; II— dehydrogenation of isopropyl alcohol and formic acid; III—dehydrogenation of isopropyl alcohol.

In the calculation of the energies of bonds formed with the catalyst, the energies of bonds between atoms in the molecules taking part in the reaction were taken from Cottrell's data [3] (cal/ mole): Q_{CH} = 90.5; Q_{OH} = 110.6; Q_{CO} = 77.1; for calculation of the values of $\underline{u}$ and $\underline{s}$: Q_{HH} = 104.2; $Q_{C=O}$ = 83.4 (second bond); $Q_{C=C}$ = 46.9 (second bond).

Table 7 gives values of activation energies, energies of bonds with catalysts, and adsorption potentials for the catalysts: No. 1—Cr_2O_3 from chromic nitrate precipitated with ammonia, and No. 2—Cr_2O_3—asbestos from chromic nitrate precipitated with sodium carbonate. For comparison, our previous results [2] with Catalyst No. 3 (Cr_2O_3 from chromic nitrate precipitated with sodium carbonate) are given. As will be seen, change in the nature of the precipitating agent, i.e. replacement of sodium carbonate by ammonia, greatly affects the activation energy for the dehydrogenation of methylcyclohexane: for Catalyst No.1, ϵ_1 = 22.0; for Catalyst No. 3, ϵ_1 = 38.0 and 38.6— a change of 16-17 kcal/mole. In the dehydrogenation of isopropyl alcohol: for Catalyst No. 1, ϵ_2 = 12.35, 11.8, and 9.8; for Catalyst No. 3, ϵ_2 = 6.4 and 6.7. There is almost no change in the activation energy for the dehydration of isopropyl alcohol: for Catalyst No. 1, ϵ_3 = 13.9, 15.2, and 15.3; for Catalyst No. 3, ϵ_3 = 13.1 and 15.0. This may occur because the reactions of dehydrogenation and dehydration of the alcohol proceed at different active centers.

The variations in the bond energies are again not constant from one catalyst to another. The variation in Q_{HK} is insignificant, the maximum variation being 4 kcal/mole; it is highest for Catalyst No. 1. The bond energy Q_{CK} varies more than Q_{HK}; for Catalyst No. 1 it is 20.0, 18.8, and 17.5 kcal/mole, and for Catalyst No. 3,11.3 and 10.0 kcal/mole; the maximum variation is 10 kcal/mole. The bond energy Q_{OK} varies greatly; for Catalyst No. 1 it is 52.9, 52.4, and 53.7 kcal/mole, and for Catalyst No. 3 it is 73.5 and 72.6 kcal/mole, a maximum variation of 21 kcal/mole. The effect of asbestos as carrier can be judged by a comparison of the results obtained with Catalysts No. 2 and No. 3. The activation energy for the dehydrogenation of methylcyclohexane over Catalyst No. 2 is ϵ_1 = 27.0 kcal/mole, and over Catalyst No. 3 it is ϵ_1 = 38.0 and 38.6 kcal/mole, i.e. greater by 11-12 kcal/mole.

For the dehydrogenation of isopropyl alcohol over Catalyst No. 2, ϵ_2 = 17.1 kcal/mole, and over Catalyst No. 3, ϵ_2 = 6.4 and 6.7 kcal/mole, i.e. less by about 11 kcal/mole for Catalyst No. 3. There was a similar change in the activation energy for the dehydration of the alcohol: for Catalyst No. 2, ϵ_3 = 28.6 kcal/mole, and for Catalyst No. 3, ϵ_3 = 13.1 and 15.0 kcal/mole, i.e. ϵ_3 is 13.6 and 15.5 kcal/mole less for Catalyst No. 3. The introduction of the asbestos carrier caused Q_{HK} to be increased by 6-7 kcal/mole, had

TABLE 7

Activation Energies ϵ, Energies of Bonds with Catalyst Q_{AK}, and Adsorption Potentials q (kcal/mole) for Chromic Oxide Prepared in Various Ways

Dehydrogenation of hydrocarbon ϵ_1	Dehydrogenation of alcohol and acid ϵ_2	Dehydration of alcohol ϵ_3	Q_{NK}	Q_{CK}	Q_{OK}	q_1	q_2	q_3	E_1	E_2	E_3
$CH_3C_6H_{11}$	i-C_3H_7OH		Catalyst № 1, Cr_2O_3, Ammonia precipitant								
22.0	12.35	13.9	55.8	20.0	52.9	151.6	184.7	148.7	29.3	16.5	18.6
22.0	11.8	15.2	57.0	18.8	52.4	151.6	185.2	147.0	29.3	15.7	20.3
22.0	9.8	15.3	58.4	17.5	53.7	151.8	188.0	147.0	29.3	13.1	20.4
$CH_3C_6H_{11}$	HCOOH	i-C_3H_7OH	Catalyst № 1, Cr_2O_3, Ammonia precipitant								
22.0	32.0	15.3	43.6	32.2	39.0	151.6	158.4	147.0	29.3	42.6	20.4
$CH_3C_6H_{11}$	i-C_3H_7OH		Catalyst № 2, Cr_2O_3—asbestos Soda precipitant								
27.0	17.1	28.6	60.7	11.9	44.9	145.2	178.2	129.4	36.0	22.8	38.1
$CH_3C_6H_{11}$	HCOOH	i-C_3H_7OH	Catalyst № 2, Cr_2O_3—asbestos Soda precipitant								
27.0	35.0	28.6	49.1	23.4	33.2	145.0	154.8	129.1	36.0	46.0	38.1
$CH_3C_6H_{11}$	i-C_3H_7OH		Catalyst № 3, Cr_2O_3, Soda precipitant								
38.0	6.4	13.1	53.9	11.3	73.5	130.4	192.6	150.0	50.6	8.5	17.5
38.6	6.7	15.0	54.7	10.0	72.6	129.4	192.0	147.3	51.5	8.9	20.2

$s_{1/2} = 165.9$; $u_{1/2} = -15.0$; $s_{2/3} = 194.3$; $u_{2/3} = -6.7$; $s_{3/3} = 162.4$; $u_{3/3} = -5.1$

little effect on Q_{CK} (a maximum increase of 1.9 kcal/mole) and caused a great change in Q_{OK}, which was 28.6 kcal/mole less for Catalyst No. 2 than for Catalyst No. 3. The value of Q_{OK} was found to be the most sensitive to the introduction of carrier.

Catalysts No. 1, 2, and 3 differed greatly from one another, as can be seen from the adsorption potentials and their positions on volcano-like curves (Fig. 7)— I is the curve for the dehydrogenation of methylcyclohexane, II is the curve for the dehydrogenation of isopropyl alcohol and of formic acid, and III is the curve for the dehydration of alcohol.

Hence, the nature of the precipitant and the carrier can greatly affect the energies of the bonds formed with the catalyst.

The effect of substituents situated outside the sphere of reaction can be seen from a comparison of data on the dehydrogenation of isopropyl alcohol and of formic acid (on Catalysts No. 1 and 2) relating to the energies of bonds formed by reacting atoms with the catalyst. The indices of these reactions are identical, but with different substituents at C values of all the bond energies changed, both for Catalyst No. 1 and No. 2 2 (Table 7), and consequently the adsorption potentials q also changed. Hence, bond energies and adsorption potentials depend not only on the nature of the catalyst, but also on the nature of the substituents in the reacting molecule. In the case of formic acid, the carbonyl group evidently has a powerful effect.

SUMMARY

1. Activation energies were determined for the dehydrogenation of methylcyclohexane, isopropyl alcohol, and formic acid and the dehydration of isopropyl alcohol and formic acid over chromic oxide prepared in different ways. From these data the energies of the bonds formed by hydrogen, carbon, and oxygen with the chromic oxide surface were found.

2. The effect of molecular structure and the method of preparing the catalyst were investigated for these reactions.

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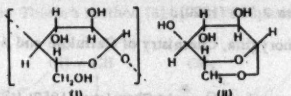
BRIEF COMMUNICATIONS

MAIN DIRECTION OF REACTION IN THE THERMAL DECOMPOSITION OF CELLULOSE IN A VACUUM

V. I. Ivanov, O. P. Golova, and A. M. Pakhomov

The chemistry of the thermal decomposition of cellulose is of great scientific interest. We have made a systematic study of the thermal decomposition of cellulose in a vacuum with the object of determining the main reactions occurring. The effects of many factors were investigated: oxidative processes, hydrolysis, molecular weight, chemical heterogeneity, the structure of the cellulose, conditions of treatment, such as temperature and residual pressure, etc.

Already in 1918, Pictet [1] carried out experiments on the thermal decomposition of cellulose in a vacuum, and from the numerous decomposition products he isolated, for the first time, the substance levoglucosan (1,6-anhydro-β-D-glucopyranose) in about 30% yield. This compound has the same chemical composition as the cellulose monomer unit (I), but in place of the hydroxyl at C-6 there is one at C-4, and the intermolecular 1,4 oxygen bridge is replaced by an intramolecular bridge in the 1,6-position (II):



(I) (II)

According to Irvine and Oldham [2], who made use of Karrer's data [3], formation of levoglucosan in the thermal decomposition of cellulose passes through the formation of glucose, which under the decomposition conditions is dehydrated to levoglucosan. This is the prevalent view on the reaction, and it is expounded in monographs on cellulose chemistry [4] and textbooks on organic chemistry [5]. Korshak [6], in a discussion of the thermal decomposition of high polymers, states that those containing hydroxy groups, including cellulose and starch, are dehydrated during thermal decomposition with formation of a mixture of products of far-reaching decomposition.

The importance of hydrolysis in the thermal decomposition of cellulose to levoglucosan was estimated in three ways: 1) some readily hydrolyzable cellulose was prepared (form of regenerated cellulose), and the thermal decomposition of this resulted in a low yield of levoglucosan; 2) experiments on the thermal decomposition of cellulose in presence of water were carried out; it was shown that the yield of levoglucosan did not increase; 3) on the view that glucose is an intermediate compound, the cellulose was impregnated with 2-20% of glucose, but the yield of levoglucosan was considerably reduced. Taking these results into account, we were able to find conditions under which the yield of levoglucosan was 60% or higher. We confirmed this yield by numerous experiments; our results are presented in the table.

Our results prove that the main direction of reaction in the thermal decomposition of cellulose in a vacuum is breakdown at the weak 1,4 glucoside links into elementary fragments that are subsequently isomerized into levoglucosan. We are carrying out further investigations on the decomposition of cellulose to levoglucosan with the object of attaining a yield close to the theoretical value. Our results open up new ways for the scientific treatment of the thermal decomposition of organic compounds, particularly carbohydrates.

TABLE

Relation of Yield of Levoglucosan to Experimental Conditions

Cellulose preparation	Experimental conditions	Yield of levoglucosan
Cotton cellulose	In a vacuum	60
Cotton cellulose	In a vacuum in presence of water	58–60
Cotton cellulose	In a vacuum in presence of glucose	25–30
Readily hydrolyzable cellulose (regenerated cellulose)	In a vacuum	5–14

SUMMARY

1. It was shown that in the thermal decomposition of cellulose the yield of levoglucosan may attain 60% or higher.

2. In the thermal decomposition of cellulose, hydrolysis, oxidation, and dehydration processes are side reactions.

3. In the thermal decomposition of cellulose in a vacuum the main direction of reaction is breakdown at 1,4 glucoside links into elementary fragments that isomerize into levoglucosan.

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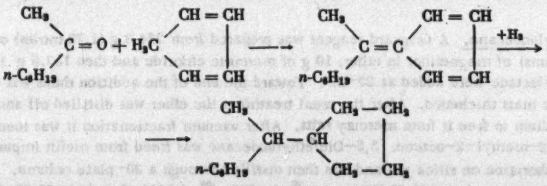
SYNTHESIS OF 2-CYCLOPENTYLOCTANE AND 5,5-DIMETHYLUNDECANE

G. A. Tarasova, G. S. Talts, and A. F. Plate

In the course of the development of methods for the investigation of ligroins in the N. D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR, various hydrocarbons were synthesized so as to provide standards for use in Raman-spectrum studies. The present paper describes the preparation of two hydrocarbons containing thirteen carbon atoms—a cyclopentane hydrocarbon with a branched side chain, 2-cyclopentyloctane, and a paraffin containing a tertiary carbon atom, 5,5-dimethylundecane. Neither of these hydrocarbons is described in the literature.

2-Cyclopentyloctane. The most convenient method of preparing monosubstituted cyclopentane homologs with a branched side chain is by hydrogenation of the corresponding fulvenes. This method has been used by several authors [1]. The best results on the hydrogenation of fulvenes (90-95% yield) were obtained by Kazansky and Terentyeva [2], who carried out the hydrogenation in the cold under a pressure of hydrogen in presence of Raney nickel. It is by this method that we prepared 2-cyclopentyloctane, starting from 6-hexyl-6-methylfulvene, which was itself prepared by Thiele's method [3] by the condensation of 2-octanone with cyclopentadiene:



5,5-Dimethylundecane. This hydrocarbon was prepared from butylmagnesium bromide and 2-chloro-2-methyloctane in presence of mercuric chloride. The necessary chloro compound was prepared from the corresponding alcohol, 2-methyl-2-octanol, which was synthesized by the Grignard reaction from hexylmagnesium bromide and acetone:

$$n\text{-}C_6H_{13}MgBr + (CH_3)_2CO \rightarrow n\text{-}C_6H_{13}C(CH_3)_2OH \xrightarrow{+HCl} n\text{-}C_6H_{13}C(CH_3)_2Cl$$

$$n\text{-}C_4H_9MgBr + n\text{-}C_6H_{13}C(CH_3)_2Cl \xrightarrow{HgCl_2} n\text{-}C_6H_{13}C(CH_3)_2\,C_6H_{13}\text{-}n$$

EXPERIMENTAL

2-Octanone. This was purified through the bisulfite compound and had the following properties: b.p. 173.0° (760 mm); n_D^{20} 1.4156; d_4^{20} 0.8186. The literature [4] gives: b.p. 172.6-173.1° (752 mm); n_D^{20} 1.41613; d_4^{20} 0.8185.

Cyclopentadiene. This was prepared by the depolymerization of its dimer, and it had the following properties: b.p. 39-42°, n_D^{20} 1.4445.

6-Hexyl-6-methylfulvene. A mixture of 178 g (1.39 moles) of 2-octanone and 100 g (1.51 moles) of cyclopentadiene was added dropwise at 10-14° to a solution of sodium ethoxide prepared from 33 g of sodium (1.43 moles) in absolute ethanol. The mixture was allowed to stand for one hour and then poured into cold water (1 liter). The upper layer was separated and washed with water to remove alkali. The fulvene, which was yellow in color, was distilled with superheated steam, separated from water, rapidly dried with calcium chloride, and vacuum-distilled; b.p. 94-96° (3mm); yield 64.1 g (44.3%).

2-Cyclopentyloctane. Shortly after being distilled, the fulvene was loaded into a rotating autoclave and hydrogenated in ethanolic solution in presence of Raney nickel at room temperature under an initial hydrogen pressure of 110 atmospheres. As soon as the pressure had fallen to fifty to sixty atmospheres, further hydrogen was pumped in. The hydrogenated hydrocarbon was steam-distilled, boiled with sodium, and repeatedly shaken with concentrated sulfuric acid and with sodium bisulfite solution. The 2-cyclopentyloctane was then passed through a silica-gel column and vacuum-distilled through a 40-plate column. The main distillate had the following properties: b.p. 236.0-236.5° (760 mm); 120.5° (19 mm); n_D^{20} 1.4475; d_4^{20} 0.8118; found MR 60.03; calculated for $C_{13}H_{26}$ MR 60.03. The yield of 2-cyclopentyloctane was about 70%.

Hexyl Bromide. Reaction between 112 g (1.1 moles) of hexyl alcohol (b.p. 157.8-158.5° (760 mm); n_D^{20} 1.4180; d_4^{20} 0.8184), 480 g of 48% hydrobromic acid, and 68 ml of concentrated sulfuric acid gave 167 g of hexyl bromide b.p. 53.7-54.7° (20mm); n_D^{20} 1.4472; d_4^{20} 1.1727. The literature [5] gives: b.p. 153.5° (746 mm); n_D^{20} 1.4478; d_4^{20} 1.1748.

2-Methyl-2-octanol. This tertiary alcohol was prepared by the Grignard reaction from hexylmagnesium bromide and acetone, which was first distilled through a 30-plate column. Three fractionations from a Favorsky flask gave an 87.5% yield of 2-methyl-2-octanol, b.p. 91.0-91.5° (24 mm); n_D^{20} 1.4281; d_4^{20} 0.8239; found MR 45.04; calculated $C_9H_{20}O$ MR 45.29. The literature [6] gives: b.p. 82-85° (20 mm); n_D^{20} 1.427.

2-Chloro-2-methyloctane. 2-Methyl-2-octanol was saturated in the cold with gaseous hydrogen chloride until the increase in weight reached the necessary value. The yield was 88.8%; b.p. 66.4-67.1° (14 mm); n_D^{20} 1.4295; d_4^{20} 0.8566; found MR 49.01; calc. for $C_9H_{19}Cl$ MR 48.63. This compound has not been described in the literature.

5,5-Dimethylundecane. A Grignard reagent was prepared from 264.3 g (1.73 moles) of butyl bromide and 46.93 g (1.93 g-atoms) of magnesium in ether; 10 g of mercuric chloride and then 157.5 g (0.97 mole) of 2-chloro-2-methyloctane were added at 20-22°. Toward the end of the addition there was noticeable evolution of gas and the mass thickened. After the usual treatment the ether was distilled off and the residue was heated with sodium to free it from mercury salts. After vacuum fractionation it was found that the head fraction contained 2-methyl-2-octene. 5,5-Dimethylundecane was freed from olefin impurities by chromatographic adsorption on silica gel and was then distilled through a 30-plate column. The main fraction had the following properties: b.p. 101.0° (16 mm); n_D^{20} 1.4272; d_4^{20} 0.7601; found MR 62.25; calc. for $C_{13}H_{28}$ MR 62.23. The yield of pure product was 34 g i.e., about 20% on the amount of 2-chloro-2-methyloctane taken.

SUMMARY

2-Cyclopentyloctane and 5,5-dimethylundecane were prepared for the first time. Their synthesis and properties are described.

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SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 6.* REACTION OF ALCOHOLS WITH ALKYL- AND ARYL-DICHLOROSILANES CONTAINING SILICON-ATTACHED HYDROGEN

M. F. Shostakovsky, D. A. Kochkin, V. L. Vinogradov, and V. A. Neterman

The reaction of alkyl—and aryl—chlorosilanes $R_nSiH_mX_{4-(n-m)}$ with alcohols has not been described in the literature. We have shown that dichloromethyl—and dichloroethyl—silanes $RSiHCl_2$ react with ethyl and butyl alcohols with formation of mono-, di-, and tri—alkoxy compounds—RSiH (Cl) (OR'), $RSiH(OR')_2$, and $RSi(OR')_3$—the predominant product depending on the amount of alcohol taken for reaction. The formation of these products can be represented as follows:

$$RSiHX_2 + R'OH \rightarrow RSiH(OR')X + HX.$$
$$RSiHX_2 + 2R'OH \rightarrow RSiH(OR')_2 + 2HX.$$
$$RSiHX_2 + 3R'OH \rightarrow RSi(OR')_3 + 2HX + H_2.$$

Thus, when the alkylhalosilane: alcohol ratio is 1 : 1, the alkoxyalkylhalosilane is formed (Equation 1), for a ratio of 1 : 2 the product is the dialkoxyalkylsilane (Equation 2), and for 1 : 3 and still lower ratios the product is the trialkoxyalkylsilane (Equation 3). In the last case the hydrogen is replaced by alkoxy. The formation of these compounds can be represented also by the following equations, which show the successive formation of these products:

$$RSiHX_2 + R'OH \rightarrow RSiH(OR')X + HX.$$
$$RSiH(OR')X + R'OH \rightarrow RSiH(OR')_2 + HX.$$
$$RSiH(OR')_2 + R'OH \rightarrow RSi(OR')_3 + H_2.$$

or

$$RSiHX_2 \xrightarrow{R'OH} RSiH(OR')X \xrightarrow{R'OH} RSiH(OR')_2 \xrightarrow{R'OH} RSi(OR')_3$$

We isolated the intermediate compounds by fractionation of the product obtained by reaction of the chlorosilane with excess of alcohol(Equation 3) or with a limited amount of alcohol (Equations 1 and 2). Our investigations indicate the high reactivity of silicon—attached hydrogen atoms in alkyl—and aryl—halosilanes. We have previously established the readiness with which such a hydrogen atom is hydrolyzed in an alkaline medium with formation of solid macromolecular products for which the following structure has been proposed:

* A previous communication by this school of authors under the same general title is also numbered 6 (Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 1062; C. B. pagination 1079)- Publisher.

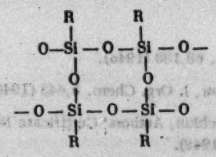
TABLE

No.	Compound	Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	C (%) found	C (%) calculated	H (%) found	H (%) calculated	Si (%) found	Si (%) calculated	Cl (%) found	Cl (%) calculated	Yield (%)
1	Butoxychloroethylsilane*	$C_6H_5SiH(Cl)(OC_4H_9\text{-}n)$	60.0 (34.5)	1.4126	0.9285	44.71	44.82	43.15 43.20	43.26	8.93 8.97	9.00	16.75 16.80	16.86	21.00 20.91	21.28	85.0
2	Dibutoxymethylsilane*	$CH_5SiH(OC_4H_9\text{-}n)_2$	80.0 (8.5)	1.4040	0.8485	55.03	55.21	56.65 56.70	56.77	11.46 11.56	11.56	14.65 14.70	14.75	—	—	50.2
3	Tributoxymethylsilane**	$CH_9Si(OC_4H_9\text{-}n)_3$	114.5 (7.5)—115 (8.0)	1.4118	0.8776	74.39	74.23	59.74 59.52	59.47	11.73 11.69	11.43	10.71 10.46	10.74	—	—	44.0
4	Dibutoxyethylsilane*	$C_2H_5SiH(OC_4H_9\text{-}n)_2$	89 (19)—90.5 (19)	1.4085	0.8465	59.58	59.84	59.04 59.11	58.81	12.08 12.01	11.76	13.37 13.43	13.75	—	—	35.0
5	Tributoxyethylsilane***	$C_2H_5Si(OC_4H_9\text{-}n)_3$	134 (16)—135 (17)	1.4140	0.8783	78.67	78.86	60.65 60.75	60.81	11.47 11.57	11.57	10.00 10.01	10.12	—	—	65.0

* Prepared for the first time.

** Reported data for tributoxymethylsilane: b.p. 115° (10 mm); n_D^{20} 1,4106; d_4^{20} 0,8775 [3].

*** Reported data for tributoxyethylsilane: b.p. 235—238°; n_D^{20} 1,4128; [4].



The high reactivity of compounds containing silicon–attached hydrogen was established by the vinylation reaction that we have developed: $RSiHX_2 + CH \equiv CH \rightarrow R(CH = CH_2)SiX_2$ [1]. It has been shown also that the hydrolysis of compounds of structure R_2SiHCl under mild conditions gives the corresponding silanols [2].

Alkoxyalkylhalo–, dialkoxyalkyl–, and trialkoxyalkyl–silanes are mobile liquids of sharp odor; they can be distilled without decomposition only in a vacuum. Alkoxyalkylhalosilanes are readily hydrolyzed and fume in the air. Fractionation of the reaction products was carried out through a 20-plate column under reduced pressure in a stream of dry nitrogen. Some of the properties of the products are given in the table.

EXPERIMENTAL

1. Preparation of Butoxychloroethylsilane $C_2H_5SiH(Cl)(OC_4H_9\text{-}n)$. Butyl alcohol (79.04 g) was added dropwise to 129.0 g of dichloroethylsilane (b.p. 74–76° (746 mm); n_D^{20} 1.4216)* contained in a three-necked flask cooled with ice and salt and fitted with dropping funnel and reflux condenser. The reaction mixture was then heated until hydrogen chloride ceased to be evolved (30–40 minutes). The boiling point of the reaction products rose to 80–90°. Fractionation of the products gave 116.8 g (85.0%) of butoxychloroethylsilane, 8.4 g of dibutoxyethylsilane, 10.4 g of tributoxyethylsilane, and 18.0 g of highly viscous resinous products.

2. Preparation of Dibutoxymethylsilane $CH_3SiH(OC_4H_9\text{-}n)_2$ and Tributoxymethylsilane $CH_3Si(OC_4H_9\text{-}n)_3$. The procedure was as described above. For the preparation of dibutoxymethylsilane, 115.0 g (1 mole) of dichloromethylsilane and 148.0 g (2 moles) of butyl alcohol were taken. Fractionation gave 95.1 g (50.2%) of dibutoxymethylsilane, 11.4 g of tributoxymethylsilane, and 50.3 g of high-boiling viscous products. For the preparation of tributoxymethylsilane 115.0 g (1 mole) of dichloromethylsilane and 225.0 g (3 moles) of butyl alcohol were taken. After addition of the alcohol the products were heated at the boil for 10-12 hours; the boiling point rose to 160–180°. Fractionation gave 5.6 g (3.7% on the amount of chloro compound) of butoxychloromethylsilane, 18.9 g (10% on the amount of chloro compound) of dibutoxymethylsilane, 115.5 g (44.0%) of tributoxymethylsilane, and 56.7 g of high-boiling resinous products. The high-boiling products were macromolecular condensed products, sparingly soluble in ethers and esters, but readily soluble in alcohols.

SUMMARY

1. It was shown that reaction between alkyldichlorosilanes containing silicon–attached hydrogen and alcohols in a ratio of 1 : 1 gives mainly alkoxyalkylhalosilanes $RSiH(Cl)(OR')$, for a ratio of 1 : 2 it gives mainly dialkoxyalkylsilanes $RSiH(OR')_2$, and for a ratio of 1 : 3 and for an excess of the alcohol it gives mainly trialkoxyalkylsilanes $RSi(OR')_3$.

2. The silicon–attached hydrogen atom of such alkylhalosilanes is readily converted into an alkoxy group.

3. A stepwise esterification scheme is proposed which is valid for alkyl–and aryl–halosilanes containing silicon–attached hydrogen.

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* Dichloromethyl–and dichloroethyl–silanes CH_3SiHCl_2 and $C_2H_5SiHCl_2$ were isolated by the fractionation of the products of direct synthesis in which the corresponding alkylchlorides were passed over a mixture of copper catalyst and silicon [5].

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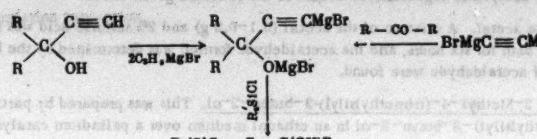
SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

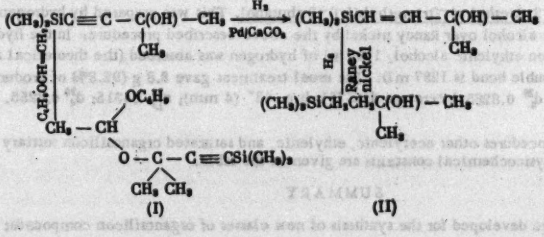
COMMUNICATION 1.* SYNTHESIS AND REACTIONS OF TERTIARY ORGANOSILICON ACETYLENIC ALCOHOLS

M. F. Shostakovsky, I. A. Shikhiev, and N. V. Komarov

The present investigation forms a continuation of our investigations on the synthesis and reactions of organosilicon γ-alcohols. In our previous investigations [1-3] we studied the synthesis and reactions of primary organosilicon γ-alcohols, and we now turn our attention to tertiary acetylenic γ-alcohols. Synthesis of these alcohols was based on the reaction of Iotsich's organomagnesium complex [4] with chlorotrialkylsilanes:



The structure of the resulting organosilicon acetylenic γ-alcohols was proved by stepwise hydrogenation and by conversion into acetals:



The physicochemical constants of the γ-alcohol (II) are in accord with reported data [5].

EXPERIMENTAL

1. Synthesis of 2-Methyl-4-(trimethylsilyl)-3-butyn-2-ol. With cooling and vigorous stirring, 42 g

* A previous communication by this school of authors under the same general title is also numbered 1 (Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 174; C. B. pagination 145)—Publisher.

(0.5 mole) of 2-methyl-3-butyn-2-ol was added to a Grignard reagent prepared from 24.3 g of magnesium and 109 g of ethyl bromide. The reaction mixture was then stirred for three hours. On the next day catalyst (0.5 g Cu_2Cl_2 + 1.0 g HgCl) was added to the reaction mixture, which was cooled while 54 g (0.5 mole) of chloroptrimethylsilane was added dropwise. The reaction mixture was then stirred for three hours at room temperature and for six hours in a hot water bath. The reaction mixture was then decomposed with 10% hydrochloric acid and neutralized with sodium carbonate solution. The ether layer was separated, washed three times with water, and dried over calcined potassium carbonate. Distillation of the solid residue remaining after removal of ether gave 48.6 g (62%) of product, b.p. 71° (8mm). It formed white needles, m.p. 42-42.5°, readily soluble in organic solvents and completely insoluble in water. It gave no precipitate with ammoniacal silver nitrate, but reacted with sodium.

Found %: C 61.56, 61.75; H 10.25, 10.24; Si 17.85, 17.75 $C_8H_{16}SiO$. Calculated %: C 61.50; H 10.32; Si 17.98.

Our results correspond to an organosilicon acetylenic alcohol of the above structure.

2. Synthesis of the Acetylenic Organosilicon Acetal. A mixture of 15.63 g (0.1 mole) of 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol and 9.1 g (0.1 mole) of butyl vinyl ether was stirred vigorously while 0.2 ml of 33% hydrochloric acid was added; the temperature of the reaction mixture rose to 86°. The reaction mixture was then heated at 90° for 30 minutes and set aside overnight, when it was neutralized with calcined potassium carbonate. Three distillations gave 16.5 g (66.4%) of product, b.p. 85-86° (3mm); n_D^{20} 1.4331; d_4^{20} 0.8541. The results correspond to an acetylenic organosilicon acetal of the structure given above.

Hydrolysis of the acetal. A mixture of the acetal (0.1-0.2 g) and 2% sulfuric acid was heated in a sealed tube in a boiling water bath for six hours, and the acetaldehyde formed was determined by the bisulfite method [8]: 93.8% and 92.1% of acetaldehyde were found.

3. Synthesis of 2-Methyl-4-(trimethylsilyl)-3-buten-2-ol. This was prepared by partial hydrogenation of 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol in an ethanol medium over a palladium catalyst prepared by Buesh's method [6]. In the hydrogenation of 10 g of the organosilicon acetylenic alcohol in presence of 10 g of catalyst, 1420 ml of hydrogen was absorbed (the theoretical amount for hydrogenation to the double-bond state is 1434 ml). The hydrogenation product was filtered from catalyst, washed free from alcohol with water, dried over sodium sulfate, and distilled. The product, amounting to 9.4 g (95.7%), had b.p. 72-73° (23.5mm); n_D^{20} 1.4430; and d_4^{20} 0.8377.

4. Synthesis of 2-Methyl-4-(trimethylsilyl)-2-butanol. This was prepared by hydrogenation of the corresponding ethylenic alcohol over Raney nickel by the above-described procedure. In the hydrogenation of 9.1 g of the organosilicon ethylenic alcohol, 1293 ml of hydrogen was absorbed (the theoretical amount for the hydrogenation of the double bond is 1287 ml). The usual treatment gave 8.8 g (92.8%) of product of b.p. 56° (6mm); n_D^{20} 1.4319; d_4^{20} 0.8265. Literature data [5]: b.p. 48° (4 mm); n_D^{20} 1.4315; d_4^{20} 0.8255.

By the above procedures other acetylenic, ethylenic, and saturated organosilicon tertiary γ-alcohols were prepared; their physicochemical constants are given in the table.

SUMMARY

1. Methods were developed for the synthesis of new classes of organosilicon compounds: tertiary acetylenic and ethylenic γ-alcohols. The presence of a triple bond in the acetylenic alcohols was proved by stepwise hydrogenation to saturated alcohols. The presence of a hydroxy group was proved by conversion into an acetal.

2. Six new organosilicon compounds were prepared.

3. In the physicochemical properties of the acetylenic, ethylenic, and saturated organosilicon alcohols obtained, the same general regularities were observed as in the case of the corresponding organic compounds [7]: the boiling points of acetylenic alcohols are higher than those of ethylenic alcohols, and the boiling points of ethylenic alcohols are lower than those of saturated alcohols. Refractive indices and densitites fall as we pass from acetylenic to saturated alcohols.

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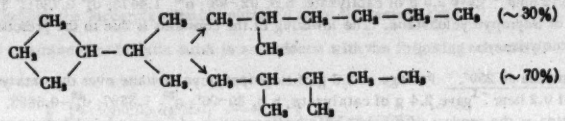
CATALYTIC HYDROGENATION OF ISOPROPYL AND ISOPROPENYL-CYCLOBUTANE

B. A. Kazansky, M. Yu. Lukina, and L. A. Nakhapetyan

Taking the examples of methylcyclobutane [1] and ethylcyclobutane [2], we have previously shown that the hydrogenolysis of cyclobutane hydrocarbons in presence of platinized charcoal proceeds to an equal extent at all bonds of the ring at about 250°. In the present investigation a hydrocarbon having a branched alkyl substituent—isopropylcyclobutane—was subjected to hydrogenolysis. It was found that, in this case also, the two possible paraffins are formed, but bond scission occurs to a greater extent at the C—C bond more remote from the substituent:



The predominance of this mode of hydrogenolysis is probably to be explained by the screening effect of the isopropyl group.

It is known that a three-membered carbon ring is reminiscent of an olefinic double bond in some chemical properties [3]. For example, this analogy is shown in the phenomenon of conjugation of a cyclopropane ring with a double bond between the first and second atoms of a side chain, the system being reminiscent of a conjugated diene [4]. The occurrence of such conjugation in the catalytic hydrogenation of isopropenylcyclopropane was recently proved by us [5]. The four-membered carbon ring is in many respects similar to the three-membered ring, and it was considered to be of interest for purposes of comparison to study the behavior of the analog of isopropenylcyclopropane—isopropenylcyclobutane—in this reaction.

It was found that, unlike isopropenylcyclopropane, isopropenylcyclobutane—both in the cold [6], and also in the vapor phase at 120°—reacts with hydrogen only at the double bond, with formation of isopropylcyclobutane. At higher temperatures this process is followed by hydrogenolysis of the ring in accordance with the scheme given above. Hence, the products of the hydrogenation of isopropenylcyclobutane and of isopropylcyclobutane in presence of platinized charcoal at 250° and at a space velocity of 0.2 hour^{-1} are identical in composition. This course of the hydrogenation reaction may be considered to prove that isopropenylcyclobutane, unlike isopropenylcyclopropane, does not have the properties of a conjugated system, that in this case no analogy exists between three—and four—membered carbon rings.

EXPERIMENTAL

Hydrogenolysis of Isopropylcyclobutane

The isopropylcyclobutane used had the following properties: b.p. 92.5° (760 mm); n_D^{20} 1.4082; d_4^{20} 0.7380; found MR 32.81; calc. for C_7H_{14} MR 32.33. The catalyst (platinized charcoal), apparatus, and experimental procedure were the same as those described previously [1,2,7]. Passage of 7.8 g of isopropylcyclobutane over the

catalyst at 250° at a space velocity of 0.2 hour $^{-1}$ gave 7.6 g of catalyzate, b.p. 89–90°; n_D^{20} 1.3897; d_4^{20} 0.6900. A further passage of the catalyzate over the platinized charcoal under the same conditions did not affect the constants.

Raman spectrum of the catalyzate *: 308 (3,b), 324 (1,b background), 386 (0), 412 (0), 424 (2), 432 (2), 463 (2,b), 480 (1,b), 499 (2,b), 556 (2,b), 712 (4), 741 (4), 751 (4), 762 (1,background), 785 (3,b), 798 (2,b,background), 823 (3,b), 848 (3,b), 873 (3,b), 895 (3,b), 917 (4,b), 956 (3,b), 969 (4,b), 986 (4), 1021 (2, b, background), 1040 (4,b), 1062 (2,b, background), 1105 (2,b), 1144 (4), 1167 (5,b), 1193 (4,b), 1222 (0), 1253 (1,b), 1284 (4,b), 1304 (5,b), 1338 (4,b), 1355 (4,b), 1382 (3,b), 1445 (8,b,background), 1464 (9,b, background).

Analysis of the Raman spectrum shows that the catalyzate was a binary mixture of 2–methylhexane and 2,3–dimethylpentane. The composition of the mixture was calculated on the basis of additivity of refractive indices and specific volumes. The mixture consisted of about 30% of 2–methylhexane and about 70% of 2,3–dimethylpentane.

Catalytic Hydrogenation of Isopropenylcyclobutane

The isopropenylcyclobutane we used had the following constants: b.p. 98.7°; n_D^{20} 1.4347; d_4^{20} 0.7743; found MR 32.36; calc. on C_7H_{12} with one double bond MR 31.86.

a) Hydrogenation at Room Temperature. This has been described previously [6]. Hydrogen adds at the double bond with formation of isopropylcyclobutane.

b) Hydrogenation at 120°. Passage of 2.1 g of isopropenylcyclobutane over the catalyst at 120° and at a space velocity of 0.2 hour^{-1} gave 2.0 g of catalyzate, b.p. 92–93°; n_D^{20} 1.4073; d_4^{20} 0.7361. These constants are close to those of isopropylcyclobutane. The lowering of the constants is due to the presence of the paraffin formed by hydrogenolysis.

c) Hydrogenation at 250°. Passage of 2.6 g of isopropenylcyclobutane over the catalyst at 250° and at a space velocity of 0.2 hour^{-1} gave 2.4 g of catalyzate, b.p. 89–90°; n_D^{20} 1.3897; d_4^{20} 0.6899. It therefore had the same composition as the product of the catalytic hydrogenation of isopropylcyclobutane at the same temperature.

SUMMARY

1. It was shown that the hydrogenolysis of isopropylcyclobutane occurs to a greater extent at the bond more remote from the substituent.

2. It was shown that in catalytic hydrogenation isopropenylcyclobutane, unlike isopropenylcyclopropane, shows none of the properties of a conjugated system.

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* The Raman spectrum was determined by Kh. E. Sterin and V. T. Aleksanyan (Spectroscopy Commission, Physics and Mathematics Society of the Academy of Sciences of the USSR), to whom we express our thanks.

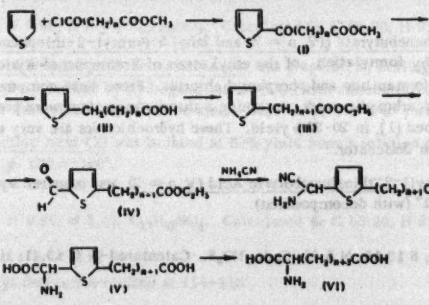
** T.p. = C. B. Translation pagination.

SYNTHESIS OF ALIPHATIC AMINO DICARBOXYLIC ACIDS FROM THIOPHENE

Ya. L. Goldfarb, B. P. Fabrichny, and I. F. Shalavina

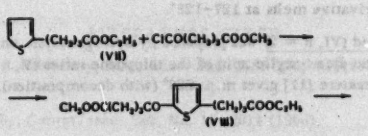
Goldfarb and Fabrichny [1] have previously described a new method for preparation of aliphatic amino acids based on the reductive desulfurization (hydrogenolysis) of corresponding thiophene derivatives with the aid of Raney nickel. Later, a short paper by Buu-Hoi and Sy [2] appeared in which the authors described what they regarded as a new method of preparing amino acids, although it was in fact based on the principle that we had proposed previously. We have recently applied the method of reductive desulfurization of thiophene derivatives to the preparation of amino dicarboxylic acids. This part of the work is not yet complete, but the appearance of the paper of Buu-Hoi and Sy—who are apparently not acquainted with our experiments—made it necessary for us to publish the incomplete results obtained up to the present time.

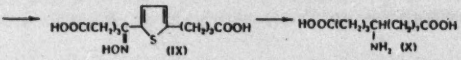
We prepared α-amino dicarboxylic acids in accordance with the following scheme:



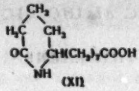
In this way we prepared 2-aminodecanedioic acid (VI, n = 2) and 2-aminoundecanedioic acid (VI, n = 3).

We have previously demonstrated the possibility of preparing aliphatic amino acids by the hydrogenolysis of oximes of keto acids of the thiophene series, the example taken being the oxime of α-oxo-2-thiopheneacetic acid [3]. We decided to make use of this method for the synthesis of 5-aminotridecanedioic acid. The route to this acid was as follows:





Hydrogenolysis of the oxime (IX) gave a mixture of 5-aminotridecanedioic acid (X) and its lactam:



By boiling this mixture with concentrated hydrochloric acid we obtained the hydrochloride of 5-aminotridecanedioic acid which we converted into the free amino acid.

EXPERIMENTAL

Methyl γ-Oxo-2-thiophenebutyrate (I, n = 2), described previously, and Methyl δ-Oxo-2-thiophenevalerate (I, n = 3) were prepared in 74-80 % yield by condensation of thiophene with methyl 3-(chloroformyl) propionate and with 4-(chloroformyl) butyrate, respectively, in benzene in presence of stannic chloride [5].

2-Thiophenebutyric Acid (II, n = 2) and 2-Thiophenevaleric Acid (II, n = 3), which have been described previously [4, 6-8], were prepared in 90% yield by reduction of the methyl esters of γ-oxo-2-thiophenebutyric and δ-oxo-2-thiophenevaleric acids by the Kizhner method, as modified by Huang-Minlon [9]. Treatment of 2-thiophenebutyric and 2-thiophenevaleric acids with ethanol saturated with hydrogen chloride at the boil gave 89-92% yields of the Ethyl Esters of 2-Thiophenebutyric (III, n = 2) [10] and 2-Thiophenevaleric (III, n = 3) Acids respectively.

Ethyl 5-Formyl-2-thiophenebutyrate (IV, n = 2) and Ethyl 5-Formyl-2-thiophenevalerate (IV, n = 3) were prepared in 75-83% yield by formylation of the ethyl esters of 2-thiophenebutyric and 2-thiophenevaleric acids with the aid of N-methylformanilide and phosphoryl chloride. From these compounds the hydrochlorides of the corresponding α-amino dicarboxylic acids containing a thiophene nucleus were prepared by the amino-nitrile reaction, as already described [1], in 20-30% yield. These hydrochlorides are very unstable and lose hydrogen chloride when dried in a vacuum desiccator.

5-[Amino (carboxy) methyl]-2-thiophenebutyric Acid (V, n = 2) was prepared by elimination of HCl from its hydrochloride; m.p. 191° (with decomposition).

Found %: C 49.44; H 5.34; S 13.15; N 5.66; $C_{10}H_{13}NO_4S$. Calculated %: C 49.41; H 5.39; S 13.18; N 5.76.

Its p-toluenesulfonyl derivative melts at 132-133°.

5-[Amino (carboxy) methyl]-2-thiophenevaleric Acid (V, n = 3) was prepared by elimination of HCl from its hydrochloride; m.p. 175° (with decomposition)

Found %: C 51.29; H 5.87; S 12.49; N 5.50; $C_{11}H_{15}NO_4S$. Calculated %: C 51.34; H 5.88; S 12.46; N 5.44.

Its p-toluensesulfonyl derivative melts at 127-128°.

2-Aminodecanedioic Acid (VI, n = 2) was prepared by hydrogenolysis under previously described conditions [1] of the corresponding α-amino dicarboxylic acid of the thiophene series (V, n = 2) in 83% yield; m.p. 233-234° (with decomposition). The literature [11] gives m.p. 228° (with decomposition).

Found % C 54.96; H 8.77; N 6.33; $C_{16}H_{19}NO_4$. Calculated % C 55.27; H 8.81; N 6.45.

The p-toluenesulfonyl derivative melts at 94–95°. The hydrochloride melts at 156–158°; when dried in a vacuum it loses HCl.

2-Aminoundecanedioic Acid (VI, n = 3) was prepared in 78% yield by the hydrogenolysis of 5-[amino (carboxy) methyl]-2-thiophenevaleric acid (V, n = 3); m.p. 226–228° (with decomposition).

Found % C 57.23; H 9.21; N 5.87; $C_{11}H_{21}NO_4$. Calculated % C 57.11; H 9.11; N 6.06.

Its hydrochloride melts at 149–151°.

Acylation of ethyl 2-thiophenebutyrate (VII) with methyl 4-(chloroformyl) butyrate in the usual way (in benzene in presence of stannic chloride with cooling) gave a 93% yield of Methyl δ Oxo-5-[3-(ethoxycarbonyl) propyl]-2-thiophenevalerate (VIII) and treatment of this with excess of hydroxylamine hydrochloride and alkali gave the oxime 5-(3-Carboxypropyl) - δ- (hydroxyimino)-2-thiophenevaleric Acid (IX). In the preparation of this oxime from (VIII) it is preferable first to hydrolyze this ester to δ Oxo-5-[3-(ethoxycarbonyl) propyl]-2-thiophenevaleric Acid (93% yield) and then form the oxime. In this way the oxime (IX) is obtained in an appreciably purer form; yield 95%.

The hydrogenolysis of the oxime (IX) was carried out under the previously described conditions [1]. A mixture of a solution of 8.2 g of (IX) in 250 ml of aqueous ammonia (about 5%) with 30 g of Raney nickel was stirred for two hours at 75–80°. Nickel was filtered off, and the filtrate was vacuum-evaporated to dryness. Drying of the residue in a vacuum desiccator gave 6.5 g of a mixture of 5-aminotridecanedioic acid and its lactam 6-Oxo-2-piperidineoctanoic Acid (XI), which was obtained in a pure state after several recrystallizations of the mixture from aqueous alcohol and reprecipitations from alkaline solution with acetic acid; m. p. 141–141.5°.

Found % C 64.80; H 9.68; N 5.97; $C_{13}H_{23}NO_3$. Calculated % C 64.70; H 9.61; N 5.80.

The Hydrochloride of 5-Aminotridecanedioic Acid was prepared by boiling the mixture of 5-aminotridecanedioic acid and its lactam, formed by hydrogenolysis of (IX), with concentrated hydrochloric acid. From 5.6 g of the mixture, 5.0 g of the hydrochloride of the amino acid, m.p. 143–145°, was obtained.

5-Aminotridecanedioic Acid (X) was isolated in 89% yield from a solution of its hydrochloride by addition of aqueous ammonia; m. p. 139.5–140°.

Found % C 59.92; H 9.86; N 5.43; $C_{13}H_{25}NO_4$. Calculated % C 60.20; H 9.72; N 5.40.

Its p-toluenesulfonyl derivative melted at 114–115°.

Found % C 58.15; H 7.76; S 7.42; $C_{20}H_{31}NO_6S$. Calculated % C 58.09; H 7.56; S 7.75.

SUMMARY

By hydrogenolysis of the corresponding thiophene derivatives, the following aliphatic amino dicarboxylic acids were prepared: 2-aminodecanedioic, 2-aminoundecanedioic, and 5-aminotridecanedioic acids.

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CURRENT EVENTS

ALL-UNION CONFERENCE ON THE APPLICATION OF ISOTOPES IN CATALYSIS

An All-Union conference on the application of isotopes in catalysis was held from March 31 to April 5, 1956, in Moscow. The conference was organized by the Institute of Physical Chemistry of the Academy of Sciences of the USSR. There were more than four hundred participants working on catalysis in the research institutes of the Academies of Sciences of the USSR and of the individual republics, of the ministries of the chemical and petroleum industries, of industrial organizations, and of teaching establishments; this number includes also scientists from the People's Democracies: China, Rumania, Hungary, Czechoslovakia, Poland, and the German Democratic Republic. Forty-four papers were read. The conference operated in two sections: Theory, and Experimental Methods.

The conference was opened by V. I. Spitsyn, Corr. Member Acad. Sci. USSR, director of the Institute of Physical Chemistry of the Academy of Sciences of the USSR. He stated that much work had been carried out in the Soviet Union in recent years on the peaceful uses of atomic energy, and one of the important fields in this work was the application of radioactive and stable isotopes in chemical investigation. Academician M. M. Dubinin gave an address of welcome on behalf of the Division of Chemical Sciences of the Academy of Sciences of the USSR.

In an introductory address, S. Z. Roginsky, Corr. Member Acad. Sci. USSR, said that this conference was the first, not only in the Soviet Union, but also in the world. The task of the conference was to make a critical examination of the results of the application of radioactive and stable isotopes to the investigation of catalysts and catalytic processes and to plan the further development of this line of work.

Greetings to the conference were conveyed by Professor Yan Chen Tsun, leader of the delegation from the Chinese People's Democratic Republic, by R. Ripan, Active Member of the Academy of Sciences of the Rumanian People's Democratic Republic and leader of the Rumanian delegation, by Professor W. Langenbeck from the German Democratic Republic, and Professor Imre Lajos from the Hungarian People's Democratic Republic.

S. Z. Roginsky's paper "Isotopes in Catalysis" indicated the wide possibilities of applying isotope methods in the investigation of catalysts and catalytic processes. The author paid particular attention to existing isotope methods for the study of active surface, and he proposed several new methods. The material obtained up to the present indicated that the active surface of catalysts is very frequently heterogeneous. The application of isotopes in the study of the microchemistry of surfaces is of immense importance, for the microchemistry frequently determines the properties of the catalyst.

The second part of this paper was devoted to an investigation of the mechanism of catalytic processes. In several cases the application of isotopes has enabled us to make great progress in the establishment of the mechanism of complex catalytic processes of great importance to the national economy and has enabled us to envisage possible ways of controlling these processes. The author stated that in the near future the mechanisms of all the main types of catalytic processes must be examined by isotope methods.

There followed a group of papers on the catalytic reactions of hydrogen. A paper by V. V. Voevodsky (Institute of Chemical Physics of the Academy of Sciences of the USSR) presented some views on the mechanism of homogeneous deuterium exchange that leads to far-reaching exchange via the deuterium exchange of free radicals in which the free valency can migrate over the radical. It is considered that the same mechanism may explain also far-reaching deuterium exchange observed under catalysis conditions. The regularities observed in deuterium-hydrogen exchange over palladium favor a mechanism of exchange through the interaction of adsorbed

hydrogen and deuterium atoms.

M. A. Avdeenko, G. K. Boreskov, and M. G. Slinko (L. Ya. Karpov Physicochemical Institute) reported an investigation on isotopic hydrogen exchange over metals differing in electronic structure, in particular over iron, cobalt, nickel, and copper, which differ in the extent to which the d levels are filled with electrons. In Group VIII specific catalytic activity at high temperatures increases with increase in the atomic number of the element and sharply diminishes as we pass to the metals of Group I, copper sub-group. For gold-platinum alloys, in which the extent to which the d levels are filled changes, the specific activity varies in a complicated way with composition. The reaction mechanism is not the same at low and at high temperatures. At low temperatures, at which the activation energy is low, an exchange mechanism via the charged intermediate complex D_3H^+ [Catalyst] is probable. Exchange at low temperatures is less specific; for example, the specific catalytic activities of platinum and gold are of the same order. The specific catalytic activities of metal catalysts of constant chemical composition but prepared by different methods are approximately constant, except in the case of platinum supported by silica gel.

In an investigation by a team of workers—A. A. Balandin, M.B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. K. Shcheglova, and E.I. Popova (Institutes of Organic Chemistry and Chemical Physics of the Academy of Sciences of the USSR)—the mechanism of the dehydrogenation of butane and butene has been studied with the aid of Neiman's kinetic isotopic method applied to the catalytic process. It was shown that butadiene is formed preferentially from butene. The rates at which butane and butene are transformed were established, and a stepwise dehydrogenation mechanism was given; the course of some side reactions was examined.

A separate session was devoted to the study of the mechanisms of reactions of catalytic oxidation of organic and inorganic compounds with the aid of the method of labeled atoms. A paper by A. B. Nalbandyan, M. B. Neiman, R. I. Mokshina, G. I. Feklisov, and A. N. Antonova (Institute of Chemical Physics of the Academy of Sciences of the USSR) described the results of an investigation on the mechanism of the thermal oxidation of methane with the aid of the kinetic isotopic method. It was shown that oxidation proceeds through the intermediate formation of formaldehyde, which is then oxidized to carbon monoxide.

An investigation of the mechanism of the oxidation of ethylene to ethylene oxide over a silver catalyst, described by L. Ya. Margolis and S. Z. Roginsky (Institute of Physical Chemistry of the Academy of Sciences of the USSR), showed that neither acetaldehyde nor formaldehyde is an intermediary in this reaction. Oxidation of olefins proceeds through non-isolated labile forms, which are tentatively considered to be charged peroxide complexes and adsorbed oxygen in the form O_2^- and O^-. The oxidation of ethylene to carbon dioxide proceeds by two independent routes via unidentified labile intermediate products. The study of oxygen exchange over V_2O_5 and Cu_2O indicated the low mobility of oxygen in the lattices of these oxides under the given conditions of reaction. Introduction of small amounts of acceptor substances into the silver catalyst alters its activity and selectivity.

A paper by G. N. Maklukhin (now deceased) and A. F. Rekasheva (Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR) discussed the mechanism of various oxidation–reduction reactions that have been studied in the liquid phase both by these authors and by others. It was established that in Meerwein–Ponndorf, Cannizzaro, and similar reactions hydrogen is transferred to a carbon atom of the compound being reduced from a covalent CH, PH, or NH of the reducing agent, and not from a hydroxyl. The transferable hydrogen does not enter into isotope–exchange reactions with the readily exchangeable hydrogen of polar solvents. It is considered that the transfer of hydrogen in these reactions proceeds intramolecularly in six- or four-membered cyclic complexes formed by the reactants. This mechanism is in accord with the low isotope effects observed for hydrogen transfer in these reactions.

A paper by Professor Wolf Langenbeck (German Democratic Republic) was devoted to a study of the mechanism of the oxidation of aliphatic hydrocarbons. It was found that, for normal hydrocarbons, combination with oxygen is equally probable for all secondary carbon atoms. The author pointed out that decisive results on the mechanism of the oxidation can be obtained only with the aid of labeled atoms—a method which he had not used.

G. K. Boreskov and L. A. Kasatkina (L. Ya. Karpov Physicochemical Institute) gave a paper on the mechanism of the oxidation of sulfur dioxide over vanadium pentoxide, investigated with the aid of O^{18} as tracer element. The heavy oxygen was introduced into the vanadium pentoxide. It was shown that the sulfur trioxide formed contained heavy oxygen in an amount corresponding to the addition of one atom of labeled oxygen per molecule.

This indicates that the primary step in the oxidation is the transfer of oxygen from the oxide catalyst to the substance being oxidized with subsequent oxidation of the catalyst by oxygen. It was possible to follow this process because of the rapidity with which oxygen diffused from the middle to the surface. S. M. Karpacheva and A. M. Rozen reported the results of a study of oxygen exchange between cupric oxide, manganese dioxide, and alumina, on the one hand, and O^{18}- labeled water, on the other. It was shown that an unequivocal interpretation of the results is impossible without special experiments, because different physical assumptions lead to identical kinetic equations.

These papers were followed by a discussion of the mechanism of catalytic oxidation, the part played by oxygen of the catalyst in the process, and also the possibility of making use of the isotopic exchange of oxygen with calcium carbonate as a geological thermometer.

In the course of the discussions, short reports of experimental results were made by B. B. Vartanyan—on the mechanism of photosynthesis, investigated by the method of labeled atoms—and by G. D. Lyubarsky—on the conductivity and catalytic activity of silver films.

A group of papers was devoted to the application of the method of labeled atoms to the determination of the mechanism of important industrial processes: synthesis of butadiene by S. V. Lebedev's method, cracking of hydrocarbons, the synthine process, etc.

O. M. Vinogradova, N. P. Keier, and S. Z. Roginsky reported the results of an investigation of the mechanism of the synthesis of butadiene. The intermediaries formed in the synthesis of butadiene from ethanol and their mutual transformations were investigated with the aid of ethanol, diethyl, ether, acetaldehyde, crotonaldehyde, and ethylene labeled with radioactive carbon. In general, the investigation confirmed the correctness of the scheme of transformations in this reaction proposed by Yu. A. Gorin, and by M. Ya. Kagan and coworkers. The behavior observed in the redistribution of hydrogen between acetaldehyde and ethanol indicates that the mechanism proposed by American workers—Quattlebaum and others—for the formation of butadiene from alcohol–aldehyde mixtures via deoxygenation of rotonaldhyde must be rejected.

In an investigationof the processes of coke formation and the polymerization of butadiene over the Lebedev catalyst, which was reported by G. M. Zhabrova and B. M. Kadenatsy (Institute of Physical Chemistry of the Academy of Sciences of the USSR), it was shown that, in presence of the Lebedev catalyst, butadiene undergoes considerable transformation, with coke formation, polymerization and hydrogenation to 2—butene. It was shown that these processes are accelerated by traces of water vapor and retarded by the introduction of alkali into the catalyst. By the use of C^{14}- labeled ethanol and butadiene, it was shown that coke is formed mainly from ethanol and polymers from butadiene.

The work of G. P. Panchenkov, Z. V. Gryaznov, V. M. Emelyanov, and L. G. Ganichenko (Moscow State University) shows that in catalytic cracking, deuterium exchange proceeds independently of the catalytic process and includes exchange between cracking products and acid centers of the catalyst. The isomerization of cyclohexane, which is considered to have an acidic mechanism, is also independent of exchange. These results are in conflict with the existing simplified concept of the mechanism of acid catalysis in cracking and isomerization. A paper by T. I. Andrianova and S. Z. Roginsky (Institute of Physical Chemistry of the Academy of Sciences of the USSR) gave the results of a study of the mechanism of the cracking of octane and hexadecane. The kinetic data indicate that the primary act consists in simultaneous breaking of the molecule into several fragments of various lengths, which then undergo secondary transformations. By the use of C^{14}- labeled ethylene and other hydrocarbons, the process of redistribution of hydrogen between ethylene and ethane, butane, and octane was investigated. In the main, redistribution of hydrogen proceeds by hydrogenation of olefins by the hydrogen of coke. The coke is formed mainly from olefins. Cracking is accelerated by the introduction of substances that decompose with formation of radicals or other active forms. Olefins, alcohols, esters, and alkyl iodides have an accelerating effect on the process.

A. Z. Dorogochinsky, N. I. Melnikov, and I. A. Shakhzadov (Grozny Petroleum Research Institute) reported results on the study of exchange between various hexane isomers and deuterium oxide adsorbed on an aluminosilicate catalyst. The exchange of n-hexane was slow, but the presence of a tertiary atom greatly accelerated exchange. The presence of a quaternary carbon atom in the molecule did not result in rapid exchange. Comparative experiments showed that the catalyst accelerated hydrogen exchange to the same degree as sulfuric acid does.

An investigation reported by O. A. Golovina, S. Z. Roginsky, M. M. Sakharov, and Ya. T. Eidus (Institute of Physical Chemistry and Institute of Organic Chemistry of the Academy of Sciences of the USSR) was concerned with the mechanism of the synthesis of hydrocarbons from a mixture of carbon monoxide and hydrogen by the Orlov–Fischer–Tropsch method. The dehydration–condensation mechanism for this process was confirmed for the first time over a typical synthine cobalt–thorium catalyst. C^{14}-labeled ethanol and acetaldehyde were used, and it was shown that, under the conditions of the reaction, acetaldehyde is hydrogenated to ethanol and that acetaldehyde gives similar results to ethanol. When labeled ethanol is present in the reaction mixture, hydrocarbon fractions of C_6 and higher are characterized by constancy of molar radioactivity, irrespective of molecular weight. It was shown that, whether ethanol is present or not, the product does not vary in composition, which is evidence in favor of the participation of ethanol in the initiation of hydrocarbon chains, but not in their rupture.

Problems of isotopic exchange, as also the theory of these processes, were given much attention at the conference, for they are continually being encountered in the investigation of catalysts and catalytic processes by isotope methods.

A. I. Shatenshtein, E. I. Zvyagintseva, E. Ya. Yakovleva, E. A. Izrailevich, Ya. M. Lozhkina, and E. V. Vedeneev (L. Ya. Karpov Institute of Physical Chemistry) studied the dependence of hydrogen exchange between hydrocarbons and solvents on the acid–base characteristics of the system investigated. It was shown that Bronsted's theory of acid–base equilibrium and catalysis gives only an approximate description of the acid-base processes investigated because these are not associated with simple proton transfer, but depend also on the charge and structural peculiarities of the substance undergoing exchange.

In the investigations of V. N. Setkina, D. N. Kursanov, and E. V. Bykov (Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR) it was shown that exchange with saturated hydrocarbons of various structures in sulfuric acid proceeds by an ion-chain mechanism with intermediate formation of carbonium ions. By study of the hydrogen exchange of carbonium ions of various structures it was shown that the carbonium carbon confers exchangeability on hydrogen atoms on a carbon atom attached to the carbonium center. The carbonium center may be able to move along a carbon chain with the result that far-reaching exchange occurs, but when a hydroxyl-group is present the displacement of the carbonium center does not occur and far-reaching exchange is absent. The presence of a positively-charged oxygen or nitrogen atom in an organic molecule, unlike that of a carbonium ion, does not confer mobility on hydrogen atoms on a neighboring carbon; this difference in properties is probably associated with the incompleted, sextet structure of the electron shell of the carbonium ion, as distinct from the oxygen and nitrogen ions, which have completed octets.

In a paper by A. I. Brodsky and N. A. Vysotskaya (Institute of Chemical Physics of the Academy of Sciences of the USSR), on the basis of much experimental material on the exchange of the oxygen of acids and of salts of various structures with the oxygen of water, a mechanism is proposed, according to which exchange passes through the intermediate stage of addition of water with formation of the ortho acid, which then decomposes either by reversal of the process or by hydrolysis, depending on the properties of the central atom; in both cases oxygen exchange will occur.

In a paper entitled "Isotopic Exchange of Oxygen between Free Hydroxyl Radicals and Water" by I. A. Kazarnovsky, N. P. Lipikhin, and M. V. Tikhomirov (L. Ya. Karpov Institute of Physical Chemistry) it was reported that observations on oxygen exchange indicate interaction between free hydroxyl radicals and water.

These papers were followed by a lively discussion.

In the discussion on papers on the mechanism of isotopic exchange it was pointed out that important advances had been made in this field in the Soviet Union and that the work described in the papers was of high standard.

In the application of labeled atoms in the field of catalysis, an important line of work is the study of the active surface of catalysts and their microchemistry. At the session devoted to this question, Imre Lajos (Hungary) gave his views on the possibility of characterizing the catalytic activities of solids by their ability to participate in isotopic exchange between their own ions and the same ions in the solution. The author showed that there is generally no parallelism because the phenomenon of exchange is complicated by recrystallization and other secondary effects. In the investigations of G. I. Korneichuk, V. A. Roiter, N. A. Stukanovskaya, B. P. Rzaeva, and Ya. V. Zhigali (Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR) it was shown with

the aid of S^{35} that in the course of the catalytic oxidation of SO_2 to SO_3 the barium-aluminum-vanadium catalyst undergoes considerable chemical change, which has a slight effect on its activity. The stability of zinc and cadmium sulfides under the conditions of the catalytic decomposition of isopropyl alcohol was studied by O. V. Krylov and E. A. Fokina (Institute of Physical Chemistry of the Academy of Sciences of the USSR). By the use of radioactive S^{35} it was shown that there is a partial conversion of sulfates into sulfides during the catalytic process. On pure sulfides dehydrogenation of the alcohol predominates, but on sulfates dehydration occurs as well as dehydrogenation. A paper by I. I. Tverdovsky and I. F. Tupitsyn (State Institute of Applied Chemistry) described the application of deuterium in the determination of the hydrogen content of a nickel catalyst. A. P. Murin and B. G. Lurye (V. G. Khlopin Radium Institute of the Academy of Sciences of the USSR) applied radioactive indicators for the investigation of the diffusion of native and foreign ions in silver halide lattices. The investigations showed that the diffusion of all these ions is determined by the general process of decompacting of the lattice. Plastic deformation produces defects, which result in an increase in the self-diffusion coefficient of the silver ion and also in the electrical conductivity. A paper by N. P. Keier (Institute of Physical Chemistry of the Academy of Sciences) was devoted to an investigation by isotope methods of the relative effects of biographical heterogeneity of the active surface and of interaction between adsorbed molecules on the laws of chemical adsorption. It was shown by direct experiments with new isotope methods that the effect of interaction or so-called "induced heterogeneity" associated with the electronic processes accompanying chemical adsorption is small and is not able to explain the departure from Langmuir adsorption observed for the activated adsorption of acetylene on nickelous oxide. In an investigation of the kinetic laws of the exchange of adsorbed C^{14}-labeled acetylene with acetylene in the gas phase which did not contain C^{14}, it was proved that the active surfaces of catalysts are extensively heterogeneous, in particular those of nickelous oxide, alumina, copper, and nickel

In the theoretical section, papers were read on the theory of isotopic effects—an important question for the application of isotope methods in any field of investigation. A paper by V. M. Tatevsky (Moscow State University) "Methods for the Statistical Calculation of Equilibrium Isotopic Exchange in the Gas Phase" contained a review of work by the author and others on this question. I. M. Lifshits and G. I. Stepanova (Kharkov Physicotechnical Institute) described their new method for determining the thermodynamic functions of a solid solution of isotopes and the laws they had found for the equilibrium of solid solutions with the gas phase.

A paper by L. S. Mayants (Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR) gave several methods for the calculation of the zero vibration energy and the frequency shift when some of the atoms of a molecule are replaced by their isotopes. These data are indispensible for the calculation of equilibrium constants of reactions in which labeled molecules take part, including isotope—exchange reactions. It was shown that, in the calculation of the shifts of characteristic frequencies of isotopically substituted molecules, the vibrations must not be attributed to individual bonds, since this leads to considerable errors. It was shown that, as a rule, the characteristic frequencies correspond to vibrations in which a whole group of bonds and angles takes part. Ya. M. Varshavsky (L. Ya. Karpov Physicochemical Institute) showed that the thermodynamic isotopic effect on the kinetics of exchange reactions is appreciable only in reactions with light isotopes, e. g. hydrogen, carbon and oxygen. The kinetics of isotopic exchange show the greater departure from a first-order law, the greater the distribution coefficient differs from unity; the greatest departure should be observed for exchange of hydrogen with deuterium and tritium. It was shown that, in the investigation of the kinetic laws of exchange reactions, the specificity of these processes must be taken into account—in particular, the equilibrium distribution of isotopes. In the discussion on these matters, it was pointed out that work on kinetic isotopic effects has not been adequately developed in the Soviet Union.

Another paper read in the theoretical section was that of M. B. Neiman (Institute of Chemical Physics of the Academy of Sciences of the USSR). The author expounded his theory of the application of the method of labeled atoms in the investigation of complex chemical processes. The application of this method was illustrated by several examples. In their paper "Isotopic Exchange between Gaseous Oxygen and the Sulfates of some Alkali Metals at High Temperature", V. I. Spitsyn and V. G. Finikov (Institute of Physical Chemistry of the Academy of Sciences) showed that the rate of isotopic exchange depends on the state of a solid reactant, in particular, on its dispersity. In a group of alkali—metal sulfates, the specific rate of exchange depends on the nature of the alkali metal as well as the particular properties of the central atom of the anion. A paper by S. N. Oziraner (Institute of Physical Chemistry of the Academy of Sciences) was devoted to a study of the kinetic laws of exchange between iodine and the iodides of lithium, sodium, potassium, and calcium. The paper gives a

theoretical interpretation of these results and an equation that satisfactorily described the laws is found.

A. N. Frumkin expounded the theory of the mechanism of the electroreduction of multi-charged anions at a metal electrode and the part played by direct electron transitions in ionic isotope–exchange reactions.

In the section on Method, a session was devoted to methods of synthesizing labeled compounds. Papers were read by S. Z. Roginsky on the general principles of introducing isotopes into organic and inorganic molecules by isotopic exchange, catalytic synthesis, biosynthesis, and the use of hot atoms (atoms of high energy); by A. I. Shatenshtein and E. A. Izrailevich on methods of synthesizing molecules containing deuterium in predetermined positions and of introducing deuterium by isotopic exchange; and by L. I. Kyukhtenko (Pisarzhevsky Institute of Physical Chemistry of the Ukrainian SSR) on the author's method of preparing certain organic compounds labeled with hydrogen, oxygen, and nitrogen isotopes.

In a second session of this section, O. V. Krylov and E. A. Fokina read a paper on the study of the acid-base surface of catalysts by a differential isotope method; they showed that the active surfaces of some oxides are homogeneous with respect to acid-base properties, for which purpose they used C^{14}-labeled cresol and aniline. D. S. Kapustin, V. A. Nogotkov-Ryutin, and M. I. Yanovsky described a method for the analysis of the specific radioactivities of the individual components of a gas mixture, which are separated chromatographically and examined by means of scintillation counter with a thin mica window in a flow-type radiometric cell in which the activity of the air-gas mixture leaving the chromatographic column is measured continuously. R. V. Kalinenko and K. P. Lavrovsky described a simple, exact method of separating a complex mixture of cracking gases by the use of chromatographic columns containing different fillings. V. A. Protashchik (Institute of Chemistry of the Academy of Sciences of the Belorussian SSR) showed that it is possible to measure the surface area of magnesia by determining its radioactivity after saturation of the surface with radioactive carbon dioxide. Two papers were concerned with the mass-spectrometric method of isotope analysis. I. P. Gragerov (Institute of Physical Chemistry of the Academy of Sciences of the USSR) showed that the isotopic composition of oxygen in various organic compounds can be determined from the isotopic composition of carbon dioxide after it has been allowed to undergo exchange with the substance under investigation. G. M. Panchenkov, I. A. Akishina, and N. N. Vasilyev (Moscow State University) described a method of investigating the emission properties of aluminosilicate catalysts.

In conclusion, the work of the conference was reviewed and a resolution was passed.

In the resolution reference is made to the progress made in the Soviet Union in the application of isotope methods for the investigation of catalysts and catalytic processes. It is pointed out, however, that the application of isotopes is mainly concentrated in the larger scientific centers (Moscow, Kiev, Leningrad) and that the amount of experimental and theoretical work is still not adequate. The extension of the use of stable isotopes is hindered by the short supply and high price of mass spectrometers and ancillary apparatus.

The conference drew the attention of the Presidia of the Academies of Sciences of the USSR and of the individual Republics, and also of the various ministries, to the necessity for a greater measure of coordination in work on the application of isotopes in catalysis and for attracting the participation of workers from branch institutes and works laboratories in this work.

The desire was generally expressed for the holding of further conferences at suitable intervals for the purpose of discussing theoretical and experimental work on the application of isotopes in catalysis.

N. Keiner

CATHODE PROCESSES OCCURRING IN THE ELECTRODEPOSITION OF THORIUM FROM FUSED ELECTROLYTES

M. V. Smirnov and L. D. Yushina

Cathode processes occurring in the electrolysis of fused salts have received far from adequate study. Many of the investigations reported were concerned with the determination of the deposition potentials of individual metals from fused electrolytes, and only a few were directly concerned with the kinetics of cathode processes.

For most fused electrolytes one of the characteristic features of their electrolysis is the high temperature of the process, which leads to the alleviation, or even complete disappearance, of kinetic difficulties in the discharge of ions at the cathode. This was shown experimentally by Karpachev and Rempel [1] for the electrolysis of fused lead and cadmium chlorides. Liquid metals separate at the cathode from the fused lead and cadmium chlorides. Liquid metals separate at the cathode from the fused chlorides without appreciable polarization. In the deposition of solid metals, polarization must again be absent when the electrolysis temperature is notably higher than the temperature at which they recrystallize. As stated by Gorbunov [2], under these conditions the atoms of the metals being deposited are so mobile that they can move quite unhindered into a position of minimum free energy on the surface of large crystals of the cathodic deposit.

The electrolysis of fused salt mixtures, unlike that of fused individual salts, is accompanied by polarization. As various workers have shown [3-8], polarization is associated with changes in concentration in layers of electrolyte in the vicinity of the electrode and is analogous to concentration polarization in aqueous solutions. When the metals being deposited are present in low concentration, limiting diffusion currents may be attained, so that the polarographic method of analysis may be extended to fused electrolytes [9-13].

At high temperatures many metals may react with higher chlorides with formation of subchlorides. This can result in the dissolution of a metal in a salt melt. The electrolysis of melts is therefore often accompanied by partial discharging of ions, which precedes the liberation of metal at the cathode and reduces current efficiency. Thus, Karpachev and Poltoratsky [14] showed that, in the electrolysis of fused lead chloride at low current density at a carbon cathode, univalent lead ions are formed:

$$Pb^{2+} + e \rightarrow Pb^{+}.$$

The cathode potential then depends on the ratio of the concentrations of Pb^{2+} and Pb^{+} ions in the electrolyte layer in contact with the electrode. This ratio is itself determined by the current density and the relative rates of diffusion of these ions in the melt. The possibility of the partial discharging of ions at the cathode has been mentioned by other authors [15-19].

It is known [20-23] that at high temperatures thorium may form lower halides. Investigations carried out in our laboratory showed that thorium dissolves in chloride melts containing Th^{4+} ions with ultimate formation of Th^{3+} ions. Laboratory experiments showed that, in the electrolysis, metal does not begin to separate immediately, but separates only on the attainment of a limiting value of the current density determined by the thorium content of the electrolyte, the temperature, the distance between the electrodes, and the accessibility of atmospheric oxygen to the melt. In an open bath, electrolysis with a current density of less than this limiting value may proceed for a long time without the separation of thorium at the cathode. At high current densities,

however, not only thorium but also alkali metal separates from mixed-salt melts.

With the object of determining what processes occur at the cathode in the electrolysis of chloride and fluoride-chloride melts containing quadrivalent thorium and alkali-metal ions, we have measured the cathodic polarization over a wide range of current densities (10^{-3} to 4 amp/sq. cm). The $ThCl_4$ concentration in the melts was varied from 0.18 to 27.8% by weight, and the temperature was varied from 600° to 800°.

EXPERIMENTAL

Thorium tetrachloride was prepared by heating briquets, formed by compressing an intimate mixture of the oxide and carbon, at 900-1000° in a stream of pure chlorine. The product was purified by two sublimations at a pressure of about 10^{-2} mm. Pure thorium tetrachloride was melted in the required proportion by weight with a eutectic mixture of lithium and potassium chlorides in an atmosphere of dry hydrogen chloride, which was blown through the melt in order to remove any possible decomposition products formed by the action of atmospheric oxygen and moisture. The salt mixtures so prepared were preserved in sealed tubes.

The measurements of cathodic polarization were made in a hermetically closed quartz cell, which is shown diagrammatically in Fig. 1. Salt mixtures of the compositions indicated above were melted in the cell under a protective atmosphere of hydrogen chloride and were then maintained under reduced pressure (about 0.1 mm) until bubbles of dissolved gases ceased to be given off. Before the measurements the cell was filled with argon, which was carefully purified from traces of oxygen and moisture.

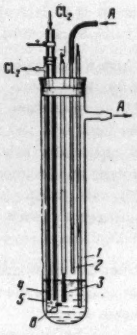

Fig. 1. Cell: 1) thermocouple; 2) tube for passage of argon; 3) cathode; 4) chlorine electrode (anode); 5) quartz test tube; 6) asbestos diaphragm.

Preliminary investigations showed that at 600-800° thorium separating at the cathode does not react appreciably with molybdenum. The polarization measurements were therefore carried out on a molybdenum wire whose surface had been freed from oxide film. The wire was immersed to a definite depth in the electrolyte, the correct depth being established by a special locator which closed a control-lamp circuit on coming into contact with the surface.

The cathode potential was measured against a chlorine electrode. This consisted of a tube of spectrographically pure carbon through which chlorine prepared by the electrolysis of fused lead chloride [24] was passed continuously. This electrode served simultaneously as anode. In order to prevent chlorine coming into contact with the cathode, the subsidiary electrode was placed in a quartz test tube having a small side tube packed with asbestos, which acted as a diaphragm. The cell was placed in a massive metal block heated in an electric resistance furnace. The temperature of the cell was controlled automatically and maintained at the desired value within not more than ±2°.

Measurements of potential difference between cathode and chlorine electrode were carried out by means of an electromagnetic oscillograph at the moment when the polarizing current was switched off. At the given current density, the cathode was polarized within 5-6 seconds. As preliminary experiments showed, this period was sufficient for the establishment of a stationary cathode potential. Breaking of the electrolysis current with simultaneous switching-in of the electromagnetic oscillograph was effected by means of a special time relay. In each experiment the cathode potential was measured for 30-40 values of current density. However, the total amount of electricity passing through the cell did not exceed 0.001 amp·hr, so that the change in the thorium tetrachloride content of the electrolyte was of no importance.

Results of Measurements and Discussion of Results

The results of our measurements are given in Figures 2, 3 and 4. The graphs are plots of relative current densities calculated for the original geometric surface of the molybdenum cathode. The polarization curves may be divided into three sections which correspond to different electrode processes determining the value of the cathode potential and the way in which it depends on current density. The first section, at low current density, corresponds to partial discharge of thorium ions without separation of metallic thorium on the cathode.

The second section characterizes deposition of metal, and the third is associated with simultaneous separation of thorium and alkali metal at the cathode.

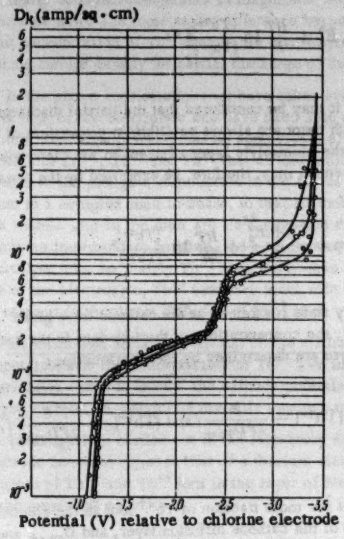

Fig. 2. Polarization of a molybdenum cathode in a chloride melt containing 0.18% by weight $ThCl_4$ (0.0133 mole % Th^{4+}) at 600° (lower curve), 700° (middle curve), and 800° (upper curve).

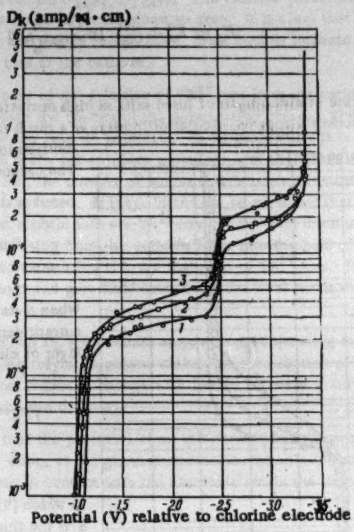

Fig. 3. Polarization of a molybdenum cathode in a chloride melt containing 2.6% by weight $ThCl_4$ (0.195 mole % Th^{4+}) at 600° (Curve 1), 700° (Curve 2), and 800° (Curve 3).

Partial Discharge of Thorium Ions at Low Cathode Current Densities. Depending on the thorium concentration and the temperature, in the current-density range 10^{-3}—10^{-2} amp/sq. cm the cathode potential lies at 0.95-1.25 v more negative than the potential of the chlorine electrode and 1.10-1.25 v more positive than the thorium electrode. With increase in current density, the potential increases very slightly in accordance with the empirical equation: $\varphi = \text{const} - b \log i$, in which, within the limits of possible errors in measurements, the coefficient before the logarithm is approximately of the value $2.3\frac{RT}{2F}$. Further increase in current density from 10^{-2} to 10^{-1} amp/sq. cm is accompanied by fairly rapid increase in cathode potential to values at which metallic thorium begins to separate.

Such a course of the polarization curve at low current density may be explained by the partial discharge of thorium ions. If we consider that the reaction of reduction of Th^{4+} ions to Th^{2+} ions occurs with intermediate formation of Th^{3+}, then with establishment of the stationary cathode potential a definite relationship between the mole-fraction concentrations of these ions will be attained in the layer adjacent to the electrode, the relationship being expressed by the thermodynamic equation:

$$\ln \frac{[Th^{4+}]_s [Th^{2+}]_s}{[Th^{3+}]_s^2} = \frac{F}{RT}(E_2^0 - E_1^0),$$

in which E_1^0 and E_2^0 are constants in the thermodynamic equations for the corresponding oxidation-reduction potentials:

$$E_1 = E_1^0 + \frac{RT}{F} \ln \frac{[Th^{4+}]_s}{[Th^{3+}]_s} \text{ and } E_2 = E_2^0 + \frac{RT}{F} \ln \frac{[Th^{3+}]_s}{[Th^{2+}]_s}.$$

In the case of electrolysis of fused salts at high temperatures it may be considered that the partial discharge of ions proceeds without particular difficulty, as a result of which there are always equilibrium proportions of thorium ions in the electrolyte layer adjacent to the electrode. The cathode potential may, therfore, be expressed by the equation:

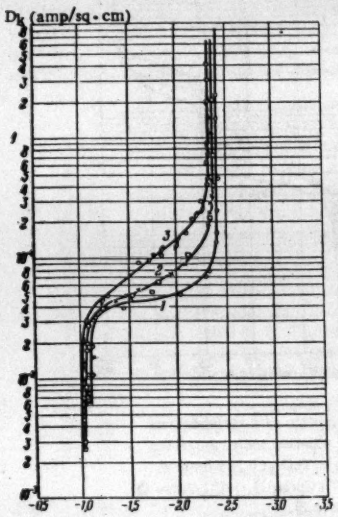

Fig. 4. Polarization of a molybdenum cathode in a chloride melt containing 27.8% by weight $ThCl_4$ (2.49 mole % Th^{4+}) at 600° (Curve 1), 700° (Curve 2), and 800° (Curve 3).

$$\varphi = \frac{E_1^0 + E_2^0}{2} + \frac{RT}{2F} \ln \frac{[Th^{4+}]_s}{[Th^{3+}]}.$$

When a stationary state is attained at the cathode for a given current density i, the concentrations of thorium ions in the cathode layer of electrolyte are determined by the relationships:

$$[Th^{4+}]_s = [Th^{4+}] - \frac{\delta}{2FD_{Th^{4+}}} i \text{ and } [Th^{3+}]_s = \frac{\delta}{2FD_{Th^{3+}}} i,$$

in which $[Th^{4+}]$ is the mole fraction of Th^{4+} ions in the electrolyte, δ is the thickness of the cathode diffusion layer, and $D_{Th^{4+}}$ and $D_{Th^{3+}}$ are the diffusion coefficients of the ions Th^{4+} and Th^{3+} in the melt.

For the stationary cathode potential we then obtain:

$$\varphi = \frac{E_1^0 + E_2^0}{2} + \frac{RT}{2F} \ln \left\{ \frac{[Th^{4+}] - \delta/2FD_{Th^{4+}} i}{\frac{\delta}{2FD_{Th^{3+}}} i} \right\}$$

or

$$\varphi = \frac{E_1^0 + E_2^0}{2} + \frac{RT}{2F} \ln \left\{ \frac{2FD_{Th^{3+}}[Th^{4+}]}{i} - \frac{D_{Th^{3+}}}{D_{Th^{4+}}} \right\}.$$

At low current density, $i \ll 2FD_{Th^{3+}}[Th^{4+}]$, and the term $D_{Th^{3+}}/D_{Th^{4+}}$ in the expression subjected to the logarithm operator may be neglected without great error. We then have:

$$\varphi = \text{const} - \frac{2.3\,RT}{2F} \log i,$$

where

$$\text{const} = \frac{E_1^0 + E_2^0}{2} + \frac{RT}{2F} \ln 2FD_{Th^{3+}}[Th^{4+}].$$

It is indeed found that such a relationship is observed experimentally at current densities of $i < 10^{-2}$ amp/sq. cm.

With increase in current density the first member of the expression under the logarithm operator diminishes and finally becomes comparable in magnitude with the second ($D_{Th^{3+}}/D_{Th^{4+}}$). The cathode potential begins to increase more and more as the difference between the terms becomes closer to zero. It is clear that increase in the concentration of Th^{4+} ions in the electrolyte, and also rise of temperature, must lead to increase in the limiting current density for partial discharge of thorium ions at the cathode.

In the above considerations we have taken account only of the diffusion of Th^{3+} ions from the cathode layer to the bulk of the electrolyte and have been able to explain the courses of the polarization curves. The diffusion of Th^{3+} ions probably has no appreciable effect on the cathode potential. In all probability it is not the simple ions Th^{4+}, Th^{3+} and Th^{2+} that diffuse through the melt, but complex groupings with the anions. With increase in the charge and reduction in the radius of an ion, the number of anions that become bound to a cation in a complex must increase, so that its mobility is reduced. It may, therefore, be expected that the least mobile ions in the melt are Th^{4+} ions, and the most mobile ions are Th^{2+} ions. Tervalent thorium ions occupy an intermediate position. As a result, the ions diffusing from the cathode layer into the bulk of the electrolyte must be mainly Th^{2+} ions, even when their concentration is lower than that of Th^{3+} ions. In the bulk of the electrolyte, Th^{2+} ions may react with Th^{4+} ions and give Th^{3+} ions, i. e., the final result will be the same as in the direct diffusion of Th^{3+} ions.

Deposition of Metallic Thorium on the Cathode. When $D_k = 0.02$-0.20 amp/sq. cm (depending on the temperature and the concentration of Th^{4+} ions in the electrolyte), a second clearly marked section of the polarization curve is found: the cathode potential almost ceases to change with further increase in the electrolysis current. A deposit of metallic thorium appears on the cathode.

Investigations carried out in our laboratory showed that the potential of an indifferent (molybdenum) electrode becomes equal to that of a thorium electrode when, at the given temperature, the relative mole fractions of Th^{2+} and Th^{4+} ions in the layer of electrolyte in contact with the electrode attain the values given by the empirical equation:

$$\log \frac{[Th^{3+}]_s}{[Th^{4+}]_s} = -10.50431 + \frac{13367}{T}.$$

With rise in temperature from 600 to 800°, the ratio $\frac{[Th^{3+}]_s}{[Th^{4+}]_s}$ changes approximately from 10^5 to 10^3. In this temperature range, therefore, thorium begins to separate on the molybdenum cathode only when the great majority of the Th^{4+} ions have been reduced to Th^{2+}. As Th^{3+} ions are formed by reduction of Th^{4+} ions from the bulk of the electrolyte, the above equation may be written as follows:

$$\log \frac{[Th^{4+}]}{[Th^{4+}]_s} = -10.50431 + \frac{13367}{T},$$

in which $[Th^{4+}]$ is the Th^{4+} concentration in the bulk of the electrolyte and $[Th^{4+}]_s$ is its concentration in the layer in contact with the cathode.

In one of our investigations it was found that the equilibrium potential of the thorium electrode with respect to Th^{4+} ions in chloride melts containing not more than 25% by weight of $ThCl_4$ varies with temperature and concentration in accordance with an empirical equation (with respect to a chlorine reference electrode):

$$E_{Th/Th^{4+}} = -2.568 + 4.742 \cdot 10^{-4} T + 0.496 \cdot 10^{-4} T \log [Th^{4+}].$$

If it is assumed that the cathode potential for the separation of metallic thorium has the equilibrium value,

i. e., is determined by the mole fraction of Th^{4+} ions in the electrolyte layer in contact with the cathode $\varphi = E^0 + \frac{RT}{4F} \ln [Th^{4+}]_s$, then it can be expressed by the equation:

$$\varphi = -3.231 + 9.952 \cdot 10^{-4} T + 0.496 \cdot 10^{-4} T \log [Th^{4+}].$$

In the table we give values of the cathode potential calculated from this equation for the temperatures and Th^{4+} concentrations that we investigated. A correction was made for the thermoelectromotive force of opposite sign between the molybdenum and carbon electrodes.

TABLE

Temperature °C	Thermo-emf	0.18 wt. % $ThCl_4$ $[Th^{4+}] = 1.33 \cdot 10^{-4}$	2.6 wt. % $ThCl_4$ $[Th^{4+}] = 1.96 \cdot 10^{-3}$	27.8 wt. % $ThCl_4$ $[Th^{4+}] = 2.49 \cdot 10^{-2}$
600	0.008	−2.52	−2.47	−2.42
700	0.009	−2.44	−2.38	−2.33
800	0.011	−2.36	−2.30	−2.24

As will be seen, the potentials corresponding to the beginning of the separation of metallic thorium on the molybdenum cathode lie on the polarization curves in positions somewhat more positive than those of the calculated values of the equilibrium potentials of the thorium electrode, particularly in melts of low thorium content. This is due to rapid depolarization by the current (of the order of 1 ma) taken from the cell by the electromagnetic oscillograph after the breaking of the polarizing current. However, when a sufficient amount of metallic thorium has collected on the cathode, the depolarization effect becomes insignificant and the cathode potential becomes identical with the equilibrium potential of the thorium electrode within the limits of experimental error (± 0.02 v). This implies that the electrocrystallization of thorium from melts is not accompanied by any appreciable polarization. In fact, its recrystallization temperature — calculated from the empirical formula $\underline{t} = \alpha \frac{t_m}{a}$, in which t_m is the melting point of the metal (1800°), $\underline{a}$ is its highest lattice parameter (5.075 A), and α is a coefficient that is assumed to be unity [25] — is 355° and considerably lower than the temperature of electrolysis.

The potential for the separation of metallic thorium is attained at current densities close to the limiting diffusion current for the discharge of Th^{4+} ions to Th^{3+} ions. If, during the deposition of thorium, the actual cathode surface remained unchanged, the limiting diffusion current for the discharge of Th^{4+} to metal should be about twice the limiting current for the partial discharge of the ions. This, however, is not observed. The cathode potential varies very little over considerably wider ranges of nominal current density (calculated on the geometric surface of the molybdenum cathode), particularly in melts of high thorium concentration. This appears to be due to the fact that, with the separation of a crystalline deposit of thorium, the active surface of the cathode changes and the nominal value of current density is no longer the actual one. As shown by the investigations of Vagramyan [26] and of Gorbunova and Dankov [27], the current density calculated for a growing (active) surface of crystalline metal deposited on the cathode from aqueous solutions remains constant during the whole electrolysis process. With increase in electrolysis current, the active surface of the deposit becomes greater in such a way that the true current density remains unchanged. An analogous phenomenon can clearly occur also in the case of the electrocrystallization of metals from fused electrolytes.

Simultaneous Separation of Thorium and Alkali Metal on the Cathode. With increase in electrolysis current, the true current density remains constant only until the transfer of Th^{4+} ions from the bulk of the electrolyte to the growing parts of the crystals of the cathode deposit of metal is assured. In other words, the development of the active surface of the cathode deposit must freely follow the growth in the electrolysis current. When it begins to lag, the cathode potential rapidly rises to −3.3-3.4 v with respect to the chlorine electrode and then remains almost constant with further rise in the current. Alkali metal appears at the cathode.

It is quite obvious that transference of Th^{4+} ions is encouraged by rise of temperature and particularly by increase in the thorium concentration of the electrolyte, as can be readily seen from the polarization curves. In a melt containing 27.8% by weight of $ThCl_4$, the cathode potential, and, therefore, the true current density, vary little for a wide range of change (more than by 50 times) in the electrolysis current. As the concentration is lowered, this range becomes narrower. We must here take acccount of the relative character of polarization curves in the region of thorium deposition. According to Vagramyan's observations [26], the measured value of the cathode potential, which rose sharrply after increase in the electrolysis current, gradually fell until a "self-adjusting" current density was established.

Various authors, including Andrieux [28] and Drossbach [19], consider that, in the electrolysis of fused mixtures containing salts of alkali or alkaline-earth metals, in the first place alkali or alkaline-earth metal separates at the cathode and this then reduces other components of the melt. Our investigations do not support an electrolysis mechanism of this sort.

Polarization of a Molybdenum Cathode in the Electrolysis of Mixed Fluoride-Chloride Melts containing Thorium. We also studied the polarization of a molybdenum cathode in a fused eutectic mixture of lithium and potassium chloride with an addition of 2.2 and 20% by weight of ThF_4. The thorium tetrafluoride was not prepared specially, but the corresponding amount of an alkali-metal fluoride was added to the chloride melt containing an equivalent amount of the tetrachloride. The results of some of the measurements are shown graphically in Fig. 5.

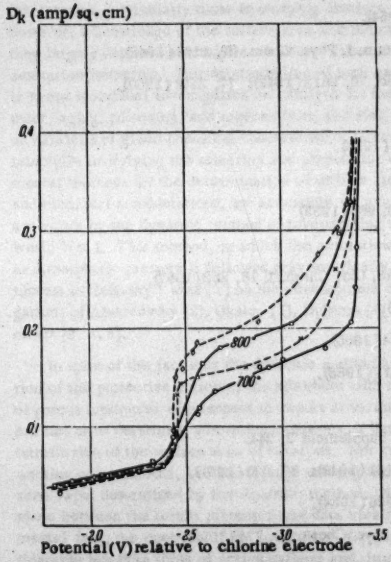

Fig. 5. Polarization of a molybdenum cathode in a mixed fluoride-chloride melt containing 2.2% by weight of ThF_4. The broken lines represent polarization in a straight chloride melt containing an equivalent amount of $ThCl_4$.

The introduction of fluoride ions into the melt in amounts equivalent to the thorium tetrachloride has no appreciable effect on the character of the cathode polarization at low current density, when partial discharge of ions occurs at the cathode. A difference appears at higher current density, particularly in the region of discharge of Th^{4+} to metal: in fluoride-chloride melts the cathode potential is displaced in the direction of more negative values and alkali metal begins to separate at lower values of the electrolysis current.

This phenomenon is probably to be attributed to the fact that, in fluoride-chloride melts, Th^{4+} ions are less mobile than in straight chloride melts. Owing to the lower radius of fluoride ions, fluoride complexes are more stable than chloride complexes; they are, therefore, formed during electrolysis as fluoride ions accumulate in the cathode layer of electrolyte, in this way rendering the subsequent discharge of Th^{4+} ions difficult. It is quite to be expected that the deposition potential of alkali metal will not change appreciably when we pass from a chloride to a mixed fluoride-chloride melt. This is to be explained by the fact that alkali metals do not form complex groupings with anions in melts.

SUMMARY

1. The polarization of a molybdenum cathode was studied at 600, 700, and 800° in a fused eutectic mixture of lithium and potassium chlorides containing 0.18, 2.6 and 27.8% by weight of $ThCl_4$ or 2.2 and 20% by weight of ThF_4 at current densities ranging from 10^{-3} to 4 amp/sq. cm.

2. It was shown that at relatively low current density (below 0.01 amp/sq. cm) reduction of Th^{4+} ions to Th^{3+} proceeds at the cathode. The cathode potential then varies with current density according to the law of

concentrational polarization. The potential for the deposition of metallic thorium is attained as the limiting diffusion current for the discharge of Th^{4+} ions to Th^{3+} is approached. During the formation of the metal deposit the true current density remains constant. When there is a low concentration of metal ions in the electrolyte, increase in the electrolysis current may result in simultaneous separation of alkali metal.

3. It was shown that introduction of fluoride ions into the melt in amounts equivalent to ThF_4 increases the potential at which metallic thorium separates at the cathode, but has no appreciable effect on the partial discharge of thorium ions at low current density and on the potential at which alkali metal separates.

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APPLICATION OF THE DYNAMIC METHOD OF MEASURING ADSORPTION OF VAPORS TO THE DETERMINATION OF THE SURFACE AREAS OF CATALYSTS

A. M. Rubinshtein and V. A. Afanasyev

The methods now in use for the determination of the surface area of solids from adsorption isotherms obtained with nitrogen, argon, or hydrocarbon vapors (butane, benzene, etc.) require the use of a high-vacuum, special optical apparatus, large amounts of mercury, and a continuous supply of liquid nitrogen; in many laboratories, particularly those in outlying districts, these requirements cannot be met. In the study of catalysts, however, a knowledge of the surface area and the character of the porous structure is very important because they largely determine catalytic activity. These are the properties which can be derived from an analysis of adsorption isotherms. The determination of such catalyst characteristics is becoming more and more necessary in every individual investigation on catalysis for the elucidation of the changes occurring during thermal treatment, aging, poisoning, and regeneration, and also, in particular, for the purpose of generalizing information on catalysts of given chemical characteristics in connection with the development of work on the scientific principles underlying the selection and preparation of catalysts. There is therefore an urgent need for experimental methods for the determination of surface area and porosity which, from the point of view of apparatus and technical considerations, are accessible for any chemical laboratory. In this connection, great possibilities are shown by the dynamic method of investigating the adsorption of organic vapors, which was developed during World War I. This method, in which the adsorption of a gas or vapor from a stream of carrier gas (air, nitrogen) at atmospheric pressure is followed gravimetrically, was one of the first to be used and was applied with great success in Zelinsky's work [1] on the development of the charcoal gas mask; we must refer also to the investigations of Alekseevsky [2], Okatov [3], Dubinin [4] and, among foreign workers, Berl and coworkers [5], and others [6, 7, 8].

In spite of the fact that the dynamic method has been widely used for the study of dynamic activity (duration of the protective action of the adsorbent with respect to the given gas or vapor) and of the adsorptive power of porous substances with respect to vapors at various partial pressures, and in spite of the fact that this method enables us to determine adsorption isotherms, it has received no application at all, until recently, for the determination of the surface area of catalysts. Not until 1951 did work of this sort appear: Fricke and Jokers [9], working with alumina, and Davis [10], working with active carbons, made use of adsorption isotherms of benzene vapor determined by the dynamic method. However, in the first of these papers [9] no comparison is made between the results presented and data obtained by other methods. Hence, owing to the paucity of experimental data, the question of the possibility of applying this method to the determination of surface areas considerably less than those of active carbons and, in even greater measure, the question of the lower limit of areas measurable with sufficient accuracy by the dynamic method remain open, as also do questions concerning purely experimental details of the method in its application to catalysts. Moreover, it is necessary to determine the extent to which a correlation exists for various values of specific surfaces between results obtained by the dynamic method and those obtained by classical adsorption methods. It is to the elucidation of all these questions that we devoted the investigation described in this paper, which has the object of drawing the attention of investigators to a convenient, simple method for determining surface area.

EXPERIMENTAL

As it was desirable to carry out the adsorption measurements by the dynamic method at ordinary temperature and pressure, the most convenient adsorbates were substances having a fairly high vapor pressure under these conditions, as high a molecular weight as possible, and a great tendency to be adsorbed. These requirements are satisfied by substances such as benzene (p_s 74.7 mm at 20°, M 78.1) and carbon tetrachloride (p_s 91.3 mm at 20°, M 153.8).

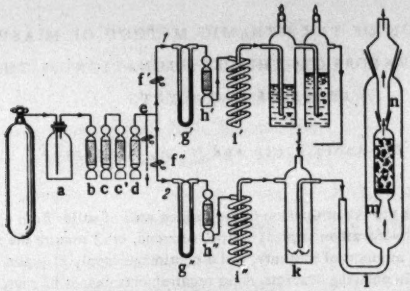

Fig. 1.

The details of the method, which are given below, were worked out in the course of the determination of the surface areas of more than fifty catalysts having specific surfaces ranging from 4 to 550 sq. m/g (determined mainly from the adsorption of benzene vapor with nitrogen as carrier); some adsorption isotherms were determined also for carbon tetrachloride.

Apparatus. The apparatus constructed for surface-area determinations by the adsorption of vapors from a gas stream was not greatly different from that generally used for the investigation of the dynamic activity and adsorptive power of solids; the apparatus is shown diagrammatically in Fig. 1. A stream of nitrogen enters a large buffer reservoir a intended for the maintenance of a steady feed, and it is dried and purified in the columns b, c, c', and d, which are filled, respectively, with active charcoal, indicator silica gel (blue), and soda lime. Preliminary crude regulation of the stream is effected by means of the tap e, which rejects excess of nitrogen into the atmosphere. Beyond the tap e the stream divides into two, which are regulated by the pinchcocks f' and f'' and measured by the flowmeters g' and g''. They pass through the protecting towers of blue silica gel h' and h'' (which trap water vapor evaporating from the flowmeters) and on to the copper coils i' and i'', in which they take up the temperature of the thermostat. One stream then passes into the evaporators j, which are filled with liquid benzene or other adsorbate; it is here saturated with the vapor and is mixed in the mixer k with the second stream, which is of pure nitrogen. By variation of the relative rates of the two nitrogen streams, the relative pressure p/p_s of adsorbate in the system can be varied from 0 to 1. From the mixer, the combined stream, which contains adsorbate vapor at a definite concentration which does not vary with time, passes to the adsorption part of the apparatus, in which there is a tube containing a weighed sample of catalyst (0.5-3 g in our experiments). The parts of the apparatus i, j, k, l are thermostated (water thermostat; ±0.1°). The velocities of the nitrogen streams were varied from 0 to 30-35 ml/min, the flowmeters being designed for this range of velocity.

Experimental Procedure and Calculations. Except when used immediately after preparation, the catalyst sample was first heated for 5-6 hours at a moderate temperature which would not cause any irreversible structural changes — preferably the temperature at which it is used in catalysis experiments or the temperature of the last stage in its preparation — for example, 400-420° for magnesia. In this process water and organic substances adsorbed during storage or in an experiment were removed. An exact amount of the sample was then weighed on an analytical balance into a previously weighed adsorption tube, which was attached through a joint to the extension piece n (Fig. 1) and lowered into the adsorber l. As will be shown below, a preliminary adsorption-desorption cycle, as recommended in the paper [10] for activated charcoals, is generally not necessary.

The tracing of the isotherm may proceed from low relative pressures, following the adsorption branch, or from high relative pressures along the desorption branch. For this purpose the nitrogen stream is turned on and regulated by means of the pinchcocks f' and f" so that the readings of the flowmeters are in accord with the required value of p/p_s, previously tabulated as a function of the relative velocities of the streams with the aid of Equation 1. After a certain time (30-60 minutes), the adsorption tube is taken out, stoppered, and weighed. For each value of p/p_s this operation is repeated until constant weight is attained. In this way the amount adsorbed is determined in grams for the given weight of sample at the given vapor pressure, so that a point on the adsorption isotherm is obtained. This procedure is repeated for a series of increasing relative pressures so as to give the whole of the adsorption isotherm. The desorption branch of the isotherm is determined by varying p/p_s in the opposite direction: for each successive point the flow of nitrogen through j is reduced and the flow of pure nitrogen is increased until p/p_s is reduced to zero.

The pressure of adsorbate vapor depends on the rate of flow of the pure nitrogen which dilutes the stream saturated with vapor at the temperature of the experiment. This relationship is expressed by the following equation [10]:

$$p/p_s = \frac{v_1}{v_1 + v_2 - v_2 \cdot p_s/p_A}, \qquad (1)$$

in which p/p_s is the relative pressure of adsorbate vapor, v_1 is the velocity of the nitrogen stream saturated with adsorbate vapor, v_2 is the velocity of the stream of pure nitrogen, p_s is the saturated vapor pressure of the adsorbate, and p_A is the atmospheric pressure (mm) (more exactly, the sum of the atmospheric pressure and the hydraulic resistance of the system (expressed in mm of mercury), which, as is shown below, may be neglected).

The isotherm is constructed in the usual coordinates: relative pressures p/p_s as abscissas, and amount adsorbed (mmole/g) as ordinates. The surface area is determined from the isotherms either graphically from the point B corresponding to the completion of a monolayer (the beginning of the linear section of the isotherm), or from the BET equation [11]; it is calculated from the equation $S = a_m \cdot \omega_0 \cdot N$, in which a_m is the amount adsorbed as a monolayer (mole/g), ω_0 is the area occupied by one adsorbed molecule on the surface, and N is Avogadro's number.

It is to be noted that of 59 isotherms which we measured by this method, 55 had the normal S-form and only 4, which were determined without prior heat treatment of samples that had been kept for a considerable time, had a concave initial portion and were unsuitable for the usual graphical calculation of the surface area. In the calculations we took the value of ω_0 for benzene to be 39 A^2 (cf. [12]). As a typical example of the isotherms obtained we give the isotherm for the catalyst MgO · NiO of specific surface 96 sq. m/g (Fig. 2); the corresponding experimental data are given in Table 1.

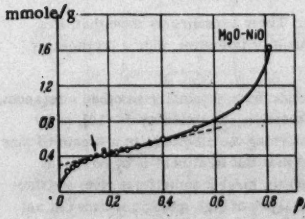

Fig. 2

Preliminary Treatment of Samples. In view of the impossibility of vacuum activation of catalysts in apparatus for the dynamic method, experiments were carried out on the cleaning of catalyst surfaces by heating and washing with adsorbate. A preliminary heating in the air greatly alters the form of isotherms obtained from catalysts that have been kept for some time after preparation and causes the isotherms to approach those obtained in a vacuum apparatus. Typical examples of the effect of a preliminary thermal treatment are shown in Fig. 3: the isotherms I are obtained with MgO catalysts that have been first heated at 420°, and isotherms II are obtained on untreated catalysts. In Fig. 3c, the triangles denote points on the isotherm determined for the catalyst MgO-7 for the adsorption of benzene vapor in a vacuum apparatus at 20°. Fig. 3c shows that, as a result of the preliminary heat treatment, the catalyst surface is adequately cleaned, this being evidenced by the almost exact coincidence of the results obtained in the vacuum apparatus and by the dynamic method. Without preliminary heat treatment the samples give isotherms that are not S-shaped; on these isotherms (Fig. 3a and 3b, isotherms II) it is impossible to distinguish the point B

and so determine the surface area graphically. Fig. 3a also shows the change in the form of the isotherm due to preliminary heating of the sample. Calculation of the specific surface of MgO-7 from the point B gave 113 sq. m/g for the dynamic method and 114 sq. m/g for the vacuum method. However, calculation from isotherm II for MgO-7 in accordance with the BET equation gave the considerably lower value of 85 sq. m/g, which indicated that part of the surface of the unheated catalyst was occupied by adsorbed substances, probably mainly

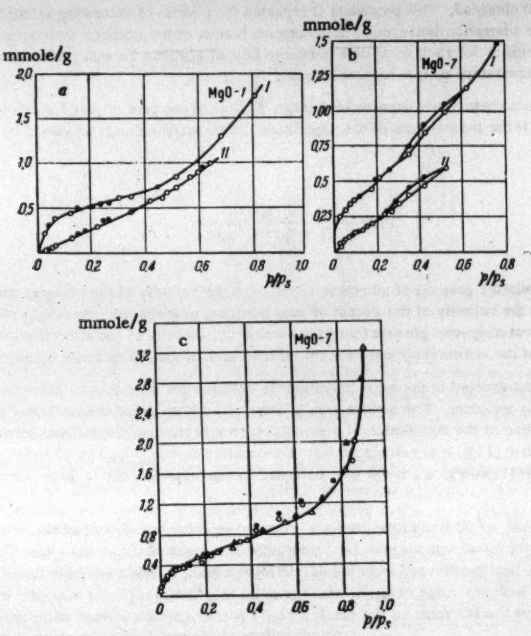

Fig. 3.

water vapor. Similar results were obtained with various other samples. These experiments show that, if a catalyst is not used immediately after its preparation for the measurement of isotherms, then a preliminary thermal treatment is essential for reliable results.

"Washing" the sample with adsorbate vapor can also clean the surface from physically adsorbed substances. This treatment can be carried out either by means of a preliminary adsorption-desorption cycle [10], or by keeping the sample in saturated adsorbate vapor in a desiccator and desorbing the adsorbate in a stream of pure nitrogen before measurement of the isotherm. Our experiments showed that this treatment is by no means essential: for samples of not very high specific surface (up to about 100 sq. m/g) it sometimes gives satisfactory results, but it has no advantage over thermal pretreatment. For catalysts of high specific surface (in our experiments, silica gel with a specific surface of 550 sq. m/g) preliminary "washing" or an adsorption-desorption cycle does not completely remove discrepancies between successively determined isotherms, which is apparently associated with the low accessibility of the fine pores to the adsorbate. The absence of irreversible hysteresis at low p/p_s for catalysts having a moderate specific surface indicates that cleaning of the surface from adsorbed gases proceeds to an appreciable extent even in the actual adsorption process.

Time Required for the Establishment of Adsorption Equilibrium. The time required for the establishment

of adsorption equilibrium not only determines the rate at which isotherms or individual points can be measured, but must be taken into account for the obtaining of reliable results. Experiments showed that the time for the establishment of equilibrium increases with increase in the specific surface of the catalyst. This is illustrated by the kinetic curves in Fig. 4. Figure 4a shows the kinetic curve for the adsorption of carbon tetrachloride

TABLE 1

Catalyst MgO-NiO (weight of sample 1.2975 g)

Velocities of nitrogen stream (ml/minute)		p/p_s	Increase in weight at adsorption equilibrium (g per 1.2975 g)	Amount adsorbed (mmole/g)
v_1	v_2			
1	30	0.036	0.0233	0.230
1	20	0.052	0.0285	0.281
1	15	0.069	0.0310	0.306
2	20	0.100	0.0350	0.345
2	15	0.128	0.0384	0.379
3	15	0.181	0.0420	0.414
4	15	0.228	0.0455	0.449
5	15	0.270	0.0481	0.475
6	15	0.307	0.0521	0.514
6	10	0.400	0.0598	0.590
5	5	0.526	0.0731	0.721
5	2.5	0.690	0.0983	0.970
10	2.5	0.810	0.1650	1.628
5	10	0.356	0.0553	0.546
3	10	0.250	0.0448	0.482
3	12.5	0.210	0.0450	0.444
2	10	0.181	0.0440	0.434
2	12.5	0.150	0.0410	0.404

vapor on a catalyst having S = 124 sq. m/g at $p/p_s = 0.036$; adsorption equilibrium was established in 40 minutes. For a catalyst having S = 204 sq. m/g (absorbate benzene) at the same relative pressure, equilibrium was attained in 3 hours; for S = 550 sq. m/g it was attained only after 7 hours (Fig. 4b). Hence, for the determination of a single point on the isotherm, 1-7 hours may be required, depending on the specific surface and character of the porosity of the sample. It should be noted that for the determination of specific surface we may confine our measurements to the section of the isotherm up to $p/p_s = 0.5$-0.6, thus considerably shortening the time spent on the determination.

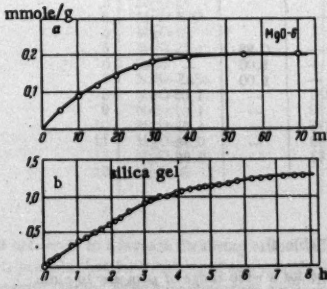

Fig. 4.

Reproducibility of Results. The data given below show that the reproducibility of results obtained by the dynamic method of measuring adsorption isotherms is quite satisfactory: in repeat determinations on various samples of the same catalyst, values of the specific surface were 176 and 195 sq. m/g for MgO-32, 113 and 108 sq. m/g for MgO-12, and 113, 124 and 129 sq. m/g for MgO-6. It will be seen that the variation in the results obtained on various samples of the sample catalyst does not exceed 10-12%, which may be regarded as quite allowable in view of the differing amounts taken and the possibility of the samples' not being completely identical.

Verification of the Results Obtained in the Present Investigation by the Dynamic Method, and the Degree of Correlation with Results Obtained by Other Methods. As will be clear from the above discussion, the results obtained by the dynamic method were verified by measuring the adsorption isotherm of benzene vapor at 20° in a standard vacuum apparatus with a quartz spring balance.*

* These isotherms were determined by B. A. Zakharov in the course of our joint work [13, 14], which was carried out simultaneously with the present investigation.

In both cases the adsorption and desorption branches of the isotherm were determined. The agreement between the results is indicated in Fig. 5, in which the circles denote points obtained by the dynamic method and triangles denote points obtained by the vacuum method (the solid points indicate the desorption branch).

As the measurements were carried out on a large number of catalysts based on magnesia (various magnesia preparations and mixed catalysts containing 10 mole % of other oxides), for the verification of the results obtained by the dynamic method we made use also of a new convenient method developed by Zettlemoyer and

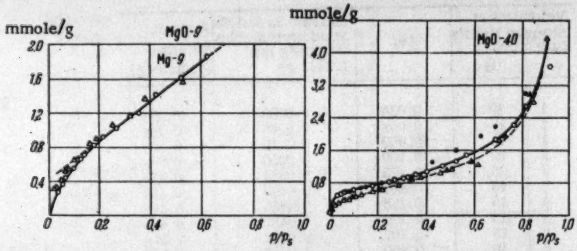

Fig. 5

Walker [15] for pure magnesium oxide – determination of the specific surface by adsorption of iodine from nonaqueous solution. It must be emphasized that, in our experiments, this method was extended to mixed magnesia catalysts, as will be seen from the tabular results given below.

All the principal experimental material is presented in Tables 2-4. These show the compositions of the catalysts, the specific surfaces determined by the dynamic (S_d), vacuum (S_v), and iodimetric (S_i) methods, and also the degree of correspondence between the results, expressed as ratios of S_d to S_v and to S_i. For convenience, the catalysts are divided into groups according to the value of the specific surface: 150 sq. m/g and

TABLE 2

No.	Catalyst	S_d	S_v	S_i	S_d/S_v	S_d/S_i
1	SiO_2	550	560	—	0.98	—
2	Al_2O_3 — MnO	241	241	—	1.00	—
3	MgO-9	204	205	—	1.00	—
4	MgO-33	200	—	187	—	1.07
5	MgO-32	195	—	183	—	1.07
6	MgO-4	179	—	178	—	1.01
7	MgO-30	179	—	186	—	0.96
8	MgO-32	176	—	183	—	0.96

higher (Table 2), 150-100 sq. m/g (Table 3), and 100-20 sq. m/g (Table 4).

Figure 5 shows that isotherms determined by the dynamic method for a wide range of p/p_s are in close accord with isotherms determined by the vacuum method; cases were found in which the "dynamic" isotherms lay somewhat higher than the "vacuum" isotherms, though were of identical form. Already from this identity or close accordance of the isotherms it follows that the two methods should give closely agreeing results. The data in Tables 2-4 show that this is in fact so: S_d/S_v is very close to unity. These results are in close accord also with results of determinations of the adsorption of iodine from carbon tetrachloride solution: S_d/S_i again

differs very little from unity. We therefore find very close agreement of results obtained by the three independent methods for catalysts having a specific surface of more than 20 sq. m/g, and we may consider that the dynamic method provides a sufficiently accurate means for the determination of the specific surface of catalysts that are unaffected, of course, by contact with air, which is almost unavoidable owing to the peculiar characteristics of the method itself (weighing of the adsorption tube, which must be taken from and replaced

TABLE 3

No.	Catalyst	S_d	S_v	S_l	S_d/S_v	S_d/S_l
1	MgO-34	146	—	140	—	1.04
2	MgO-40	146	124	—	1.18	—
3	MgO — NiO № 4	139	—	140	—	0.99
4	MgO-6	113	117	110	0.97	1.03
5	MgO-31	127	—	140	—	0.91
6	MgO-8	124	117	110	1.06	1.13
7	MgO-1	117	130	131	0.90	0.90
8	MgO-7	113	114	108	0.99	1.05
9	MgO-12	110	106	126	1.04	0.87
10	MgO-29	106	—	115	—	0.92
11	MgO-41	99	—	98	—	1.01
12	MgO — NiO № 2	96	—	98	—	0.98

in the apparatus, with removal and replacement of stoppers). The worst results were obtained with catalysts having a specific surface of about 20 sq. m/g, as will be seen from Table 4, Nos. 10-12; moreover, for four samples with specific surfaces of up to 20 sq. m/g, values of S_d/S_v of about 0.6 were obtained. The causes of this are not altogether clear to us; we may only suppose that in these latter cases the preliminary treatment

TABLE 4

No.	Catalyst	S_d	S_v	S_l	S_d/S_v	S_d/S_l
1	MgO-23	89	—	84	—	1.06
2	MgO-24	78	53	78	1.47	1.00
3	MgO-NiO	58	—	57	—	1.02
4	MgO-18	56	52	52	1.08	1.08
5	MgO-22	49	—	54	—	0.91
6	CrSe	39	38	—	1.03	—
7	NiSe-ZnSe	35	23	—	1.52	—
8	MgO-36	28	—	28	—	1.00
9	NiSe	23	24	—	0.96	—
10	MgO-46	22	—	26	—	0.85
11	MgO-47	22	—	16	—	1.37
12	MgO-39	22	—	17	—	1.29
13	MgO-38	20	—	20	—	1.00

did not result in adequate cleansing or that some of the pores were inaccessible to the large benzene molecules. It is possible that for catalysts of low specific surface these small pores may be satisfactorily determined by the dynamic method when supplementary methods of preliminary treatment are employed; this matter is being investigated further.

Simultaneous Measurement of Several Adsorption Isotherms. In the interests of economy in time and greater productivity from the apparatus, we carried out a series of experiments in which benzene vapor adsorption isotherms were determined simultaneously on six catalyst samples. For this purpose the adsorption part of

the apparatus was constructed as shown in Fig. 6. Experiments showed that, in this apparatus, adsorption equilibrium is attained considerably more slowly than when a single tube and sample is employed; the results, however, are just as accurate as those described above. Steps can be taken to combat the retardation of the establishment of adsorption equilibrium when several isotherms are determined simultaneously by diminishing the dead space in the adsorption part of the apparatus and somewhat increasing the linear velocity of the nitrogen stream containing benzene vapor, i. e., the combined stream leaving the mixer k (Fig. 1). The use of an apparatus containing several adsorption tubes can be recommended for catalysts having low or moderate specific surface: in this case a considerable economy in time can indeed be obtained.

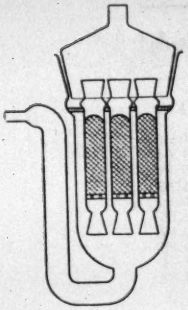

Fig. 6

Sources of Possible Error. For a given weight of catalyst and a given adsorbate, the accuracy of the results depends mainly on the accuracy with which the required pressure of vapor is established in the stream (i. e., on the accuracy of the flowmeters and of the maintenance of a constant rate of flow), on the accuracy of weighing, and, to a much lower degree, on the accuracy of thermostating and the variation in atmospheric pressure. Simple calculations that we have made for $p/p_s = 0.525$ show that, for a change in atmospheric pressure from 730 to 760 mm, the value of p/p_s calculated from Equation 1 changes by only 0.0015. For this reason we may make a preliminary calculation of the ratio of the velocities of the nitrogen streams necessary for the establishment of a given value of p/p_s. These results show that the hydraulic resistance of the system, which amounts to 10-20 mm, can be neglected and p_A can be assumed to be equal to atmospheric pressure without appreciable distortion of the results. For thermostating we used an ultrathermostat, and we considered that the temperature was constant to within 0.1°; a somewhat greater variation in temperature is permissible and very simple thermostats can be used. The errors due to the two causes examined are less than those of the measurement of rates of flow of nitrogen with the flowmeters; in our experiments these measurements were accurate within 0.08-0.1 ml/minute, so that for medium values of p/p_s this error in the measurement of rates leads to an error of 0.005 in the value of p/p_s, and for low values of p/p_s it leads to an error of up to 0.01. It is therefore necessary to select an calibrate the flowmeters with the greatest care, and it is most important to regulate the nitrogen stream very accurately and to maintain the liquid levels constant for each value of p/p_s.

When the usual analytical balance (accurate within $2 \cdot 10^{-4}$ g) is used, then for 1 g of adsorbent with benzene as adsorbate the sensitivity of the method is $2 \cdot 10^{-4}$ mmole/g, which corresponds to an error in the determination of the surface of about 0.05 sq. m/g, which may be completely neglected.

All these determination errors, which are peculiar to the method itself, are negligibly small in comparison with the error introduced in the choice of the value of the molecular area ω_0 (for example, for benzene ω_0 is taken to be 39 A^2 in some papers, but 32.3 and even 23 A^2 in others), as will be clear from the formula $S = a_m \cdot \cdot \omega_0 \cdot N$. However, if it is not required to determine the "absolute" value of the surface area, then for a series of determinations it is quite allowable to use any well-founded value of ω_0.

In conclusion, we must point out that, as comparisons of surface area and its effect on activity have meaning only for catalysts of identical chemical nature — of the same type with respect to composition — for catalysis the greatest interest is presented not by the absolute value of the surface area, but the relative specific surfaces within a series of catalyst samples. The accuracy of determinations made by the dynamic method is therefore quite adequate for the evaluation of catalysts on the basis of specific surface.

SUMMARY

1. It was shown that adsorption isotherms for benzene vapor can be determined at ordinary temperature and pressure by a method which, from the point of view of apparatus, is accessible to any chemical laboratory and which can be successfully applied to the determination of the surface area of catalysts with results that are in close accord with those obtained with the aid of high-vacuum apparatus.

2. For specific surfaces ranging from 20 sq. mμg upwards, the discrepancies between the results obtained by these two methods do not exceed 10%. The same degree of correlation is observed both for pure and mixed magnesia catalysts investigated by these two methods and also by the method [15].

3. It was shown that method [15] can be applied to mixed catalysts based on magnesium oxide.

4. The sources of possible error and methods of preparing samples for the determination are discussed.

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HEAT OF ADSORPTION OF BENZENE VAPOR ON CARBON BLACKS
THERMODYNAMICS OF THE PROCESS AND THE ADSORPTION FORCES

N. N. Avgul, G. I. Berezin, A. V. Kiselev and I. A. Lygina

In a previous investigation on the heats of adsorption of hydrocarbons, the heats of adsorption of hexane on oxidized and graphitized carbon blacks were determined [1]. The present paper is concerned with the adsorption of benzene vapor on the same carbons. The molecules of the two hydrocarbons contain equal numbers of carbon atoms, but they differ greatly in structure, so that the determination and comparison of the heats of adsorption of these hydrocarbons and the theoretical calculations of the adsorption energies are of great interest for the study of the nature of adsorption; they are also of practical importance for the understanding of the chromatographic separation of hydrocarbons. For convenience of comparison, the scheme adopted for the discussion and calculations is the same in this paper as in the previous one [1].

EXPERIMENTAL

The same carbon samples were used as in the previous investigation [1]. The original material was the carbon black "Sferon-6," which was evacuated for 12 hours at about 900°. This sample was considerably oxidized at the surface. The graphitized sample was prepared as follows: the same Sferon-6 was evacuated for 6 hours at about 950° and then heated further at 1700° in a stream of hydrogen in a Tamman furnace for 90 minutes. The sample was cooled in a stream of hydrogen. In the course of this treatment there was an increase

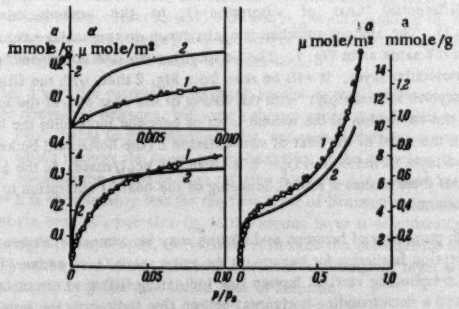

Fig. 1. Adsorption isotherms for benzene vapor (1) and hexane (2) on graphitized Sferon-6 at 20°. The solid points refer to desorption.

in the size of the crystallites forming the particles of the carbon, the surface of which became more homogeneous.

After the investigation of these samples in experiments on the heats of adsorption of hexane vapor [1], they were again evacuated in the thimble of the calorimeter at 280°, after which the adsorption of benzene vapor was measured. The experiments were carried out at 20°. The heats of adsorption were measured with the aid of an automatic constant heat-exchange calorimeter (1953 model) – an improved model of the calorimeter described in [2]. The adsorption was measured by the volumetric liquid method with the aid of vacuum

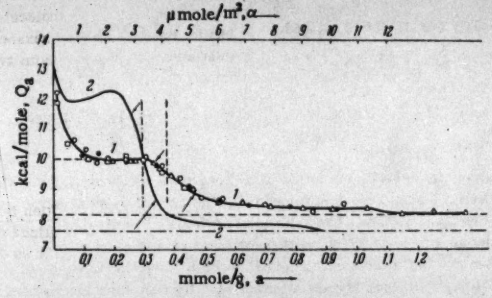

Fig. 2. Relation of the differential heats of adsorption of benzene (1) and hexane (2) vapors to the amounts adsorbed on graphitized carbon.

microburet similar to that described in [3].

The isotherm for the adsorption of benzene vapor on graphitized carbon is given in Fig. 1 (curves with points); plots against three different p/p_s scales are shown. As the surface area of the sample is known [1], not only the relative values a (mmole/g) are given, but also the absolute adsorption α (μmole/sq. m). Three agreeing series of measurements were made; the different markings of the points correspond to the different series. The adsorption isotherm has an S shape. The desorption isotherm coincides with the adsorption isotherm right down to very low relative pressures.

The relation of the differential heat of adsorption Q_a to the amount adsorbed is shown for benzene vapor in Fig. 2 (Curve 1). The amount adsorbed is again shown on two scales – relative and absolute. The denotation of the points is the same as in Fig. 1. The vertical broken line corresponds to the covering of the surface by a compact unimolecular layer. It will be seen from Fig. 2 that, with the filling of the first 25% of the surface, the heat of adsorption falls sharply; with the filling of the next 50% of the surface it remains constant; and on transition to the adsorption of the second layer of benzene molecules the heat of adsorption falls steeply. It does not attain the level of the heat of condensation L (the horizontal broken line); the true heat of adsorption of the second layer of molecules $Q_a - L$ is about 0.5 kcal/mole. In the adsorption of the third layer of benzene molecules there occurs a further lowering of the heat of adsorption to values close to the heat of condensation of benzene.

In order that the adsorption properties of benzene and hexane may be compared, Figures 1 and 2 show also the adsorption and heat of adsorption isotherms for hexane on the same graphitized carbon [1] (Curves 2, without points). In Fig. 2 there is a corresponding vertical broken line indicating filling of the surface with a compact unimolecular film of hexane, and a corresponding horizontal broken line indicating the level of the heat of condensation of the vapor. It will be seen from Fig. 1 that at low relative pressures the adsorption isotherm of hexane lies considerably higher than that of benzene. In the vicinity of $p/p_s = 0.05$ the isotherms intersect and the adsorption of benzene becomes greater than that of hexane. Above $p/p_s = 0.2$ the isotherms are approximately affine.

The cause of the great difference in the adsorbabilities of benzene and hexane in the initial part is readily seen when the heats of adsorption are compared. It will be seen from Fig. 2 that in the the middle part of the

section concerned with the filling of a unimolecular layer, which characterizes the homogeneous part of the surface, the heat of adsorption of hexane is 2.1 kcal/mole greater than that of benzene. The value Q_a is here 12.1 kcal/mole for hexane and 10.0 kcal/mole for benzene. The true heats of adsorption $Q_a - L$ differ still more: the difference is almost 2.5 times as much. The intersection of the adsorption isotherms in the region of the completion of a unimolecular layer above $p/p_s = 0.05$ is to be explained by the fact that the area occupied by a molecule in a compact monolayer is less for benzene than for hexane. In the region of multimolecular adsorption the isotherms are affine and the ratio of the amounts adsorbed by the two substances is close to the ratio of the values of ω_0 for these hydrocarbons (see below).

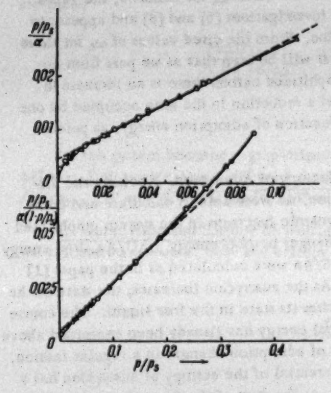

Fig. 3. Absolute adsorption isotherm for benzene vapor on the graphitized carbon Sferon-6 in the coordinates of the Langmuir equation (above) and in the coordinates of the BET equation (below).

Thermodynamics of Adsorption in the System Benzene — Graphitized Carbon

1. Equation of the Absolute Adsorption Isotherm. As in the case of the system hexane — graphitized carbon [1], for the system benzene — graphitized carbon we used the theoretical equations of Langmuir and BET and also Halsey's equation. Figure 3 shows the absolute adsorption isotherm of benzene vapor on graphitized carbon in the coordinates of the linear forms of the first two equations. It was found that Halsey's equation was not applicable in this case. It will be seen from the upper part of Fig. 3 that Langmuir's equation is obeyed in the range of p/p_s from 0.01 to 0.06, which corresponds to a change in the amount adsorbed from 1.4 to 3.5 μmoles/sq. m. Figure 2 shows that in this range the heat of adsorption remains constant, which is a theoretical prerequisite for the validity of this equation. The Langmuir graph gives the adsorption equilibrium constant K_1 as 51 and the density of the unimolecular layer as $\alpha_m = 4.60$ μmoles/sq. m.

The BET equation is valid over a wider range of relative pressures, extending in the direction of higher p/p_s (p/p_s values ranging from 0.01 to 0.20, the amounts adsorbed ranging from 1.4 to 4.5 μmoles/sq. m). The BET graph gives values of the constants of $C = 56$ and $\alpha_m = 4.12$ μmoles/sq. m. Hence, in meaning, the constants K_1 and C are the same quantity [1], and the values of the constant α_m determined from the two equations are very similar, the difference being less than 10%.

Comparison of Fig. 3 with the corresponding graph for the system hexane — graphitized carbon [1] shows that both equations are obeyed by benzene, but over a shorter range than for hexane. This may be due to the following two causes. First, owing to their compactness, benzene molecules are more sensitive to residual surface heterogeneity, which narrows the range of applicability of the equations in the low p/p_s region. Second, in the case of the BET equation the range of high relative pressures is narrowed because the value of the true heat of adsorption $Q - L$ is considerably less for the first layer of benzene molecules than for the first layer of hexane molecules, but the heat of adsorption Q_a of the second layer is considerably higher as a percentage of the heat of adsorption of the first. Hence, in the case of hexane the prerequisite of the validity of the BET equation — the equality of the heat of adsorption of a second or subsequent layer with the latent heat of condensation L — is more closely fulfilled than in the case of benzene.

On the basis of the BET equation we estimated the area occupied by a benzene molecule on graphitized carbon to be 40.3 A^2. This value is closely in accord with that given in the paper [4] on the carbon "Graphon" (41 A^2). Hence, in the adsorption layer the benzene molecule is oriented parallel to the carbon surface. The area ω_0 for a benzene molecule adsorbed on ungraphitized carbon black was determined in the investigations [5] and [6]. In the first of these investigations the value $\omega_0 = 46.5$ A^2 was obtained, and in the second $\omega_0 = 44.5$ A^2. We determined the adsorption isotherm for benzene vapor on the original sample of carbon by a more exact method than had been used in the investigations [5] and [6]. The adsorption isotherm on this sample

is represented in Fig. 4 in the usual coordinates and also in the coordinates of the BET equation. The adsorption isotherm is in accord with the BET equation in the p/p_s range 0.02-0.3 and in the adsorption range 0.2-0.55 mmole/g. From the BET graph we obtain values of constants of $C = 35$ and $a_m = 0.408$ mmole/g. As the specific surface of this sample of carbon is known [1], it was possible to calculate ω_0 for benzene, the value obtained being 44.0 A^2. This value is close to that obtained in the investigations [5] and [6] and appears to be the most accurate value. From the cited values of ω_0 for these samples of carbon black it will be seen that as we pass from ungraphitized carbon to graphitized carbon there is an increase in the energy constant C and a reduction in the area occupied by one molecule, i. e., ω_0 is a function of adsorption energy, as pointed out in the paper [7].

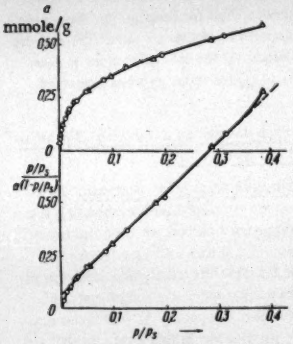

Fig. 4. Adsorption isotherm for benzene vapor on the original Sferon-6 (above) and the same isotherm in the coordinates of the BET equation (below).

2. Work, Heat and Entropy of Adsorption. Knowing the differential heats of adsorption, we were able to calculate and compare changes in thermodynamic functions in the system graphitized carbon–benzene. The changes in total energy $\partial\Delta U/\partial a$, free energy $\partial\Delta F/\partial a$, and entropy $\partial\Delta S/\partial a$ were calculated as in the paper [1] and are given in Fig. 5. As the adsorption increases, the state of the adsorbed benzene approaches its state in the free liquid. The course of the curve for the internal energy has already been examined above (Fig. 2). The free energy of adsorption changes in a regular fashion. The curve for the the differential of the entropy of adsorption has a complex wave-like form. At the start of the formation of the first surface layer the entropy is positive. In this region the entropy passes through a maximum and then falls and passes over to the negative side as the surface fills. This fall continues until the formation of a compact monolayer is complete. In the region of transition to adsorption in the second layer the entropy curve rises, after which as the second layer gradually fills a reduction in entropy is again observed.

The results indicate that the mobility of benzene molecules at the start of the formation of the first layer is greater than in the free liquid. As the surface becomes filled the mobility of benzene molecules diminishes sharply, and as the formation of a compact monolayer is approached it becomes less than in the free liquid. Molecules adsorbed in the rarefied second layer are again more mobile than in the liquid. With further adsorption the state of the benzene becomes close to its state in the free liquid. The early maximum on the curve is probably to be associated with residual heterogeneity of surface, which reduces the mobility of benzene molecules somewhat.

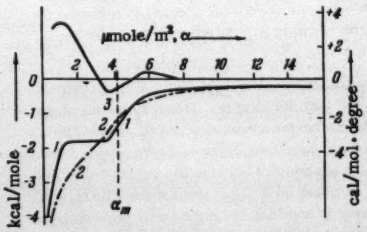

Fig. 5. Relation of changes in thermodynamic functions in the adsorption of benzene vapor on graphitized carbon to the absolute value of the adsorption.
Curves 1 and 2: $\frac{\partial\Delta U}{\partial a}$ and $\frac{\partial\Delta F}{\partial a}$ (scale on left);
Curve 3: $\frac{\partial\Delta S}{\partial a}$ (scale on right).

Comparison of the adsorption entropy curve of benzene on graphitized carbon with the corresponding curve for hexane [1] shows that their courses are extremely similar, but the curve for benzene is considerably displaced toward the positive region, as compared with the hexane curve. This indicates the greater mobility of benzene molecules in the adsorbed layer, which is in keeping with the lower heat of adsorption. This will be seen clearly from a comparison of the values of the mean molar change of entropy in the adsorption of the first layer of adsorbate. This is – 2.6 cal/mole degree for hexane and + 1.6 cal/mole·degree for benzene, which is greater, therefore, by 4.2 entropy units.

3. Standard Values of Free Energy, Total Energy, and Entropy of Adsorption. For comparison with other adsorbates in investigation [1], the values of the thermodynamic functions at a given surface coverage (θ) were examined. A coverage of 50% was taken as the standard state. The standard values of the functions ($\theta = 0.5$) are then:

$$\left(\frac{\partial \Delta U}{\partial a}\right)_{\theta=0.5} = \Delta U^0, \left(\frac{\partial \Delta F}{\partial a}\right)_{\theta=0.5} = \Delta F^0, \left(\frac{\partial \Delta S}{\partial a}\right)_{\theta=0.5} = \Delta S^0.$$

For the system benzene – graphitized carbon: $Q_a = 10.0$ kcal/mole; $\Delta U^\circ = -(Q^\circ_a - L) = 1.85$ kcal/mole; $\Delta F^\circ = -2.40$ kcal/mole; $\Delta S^\circ = +1.9$ cal/mole·degree. The corresponding values for hexane are $Q^\circ_a = 12.1$ kcal / mole, $\Delta U^\circ = -4.5$ kcal/mole, $\Delta F^\circ = -3.65$ kcal/mole, $\Delta S^\circ = -2.90$ cal/mole·degree.

4. Work, Heat and Entropy of Wetting. With the aid of the total energy and free energy curves (Fig. 5), we calculated the work, heat and entropy of wetting [1]:

$$\frac{A_w}{s} = -\int_0^{a_s} \frac{\partial \Delta F}{\partial a} da + \sigma, \qquad (1)$$

in which σ is the surface tension of benzene (28.1 ergs/sq. cm). Graphical integration gives 86.2 ergs/sq. cm for the work of wetting:

$$\frac{Q_w}{s} = -\int_0^{a_s} \frac{\partial \Delta U}{\partial a} da + \varepsilon, \qquad (2)$$

in which ϵ is the total surface energy of benzene (65.9 ergs/sq. cm).

Graphical intergration gives $\frac{Q_w}{s} = 118$ ergs/sq. cm. This value is, in graphites, 114 and 117 ergs/sq. cm [8]. At 20° the work of wetting is 73% of the heat of wetting. The entropy of wetting is −0.109 ergs/sq. cm·degree.

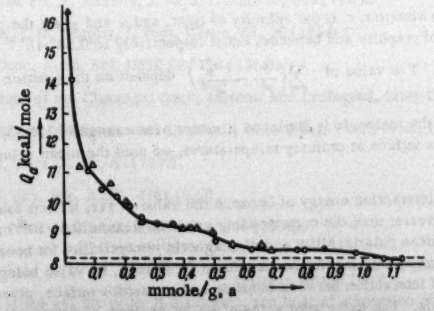

Fig. 6. Relation between the differential heat of adsorption of benzene vapor and the amount adsorbed on the original Sferon-6 carbon. The broken line is the heat of condensation.

We measured also the differential heat of adsorption of benzene vapor on the original sample of oxidized carbon (Fig. 6). It falls continuously as the surface coverage increases, this being due to the heterogeneity of the surface of ungraphitized carbon. Graphical integration gives 125 ergs/sq. cm as the heat of wetting of this carbon. From this it is clear that although the courses of the curves for differential heat of adsorption are quite different for graphitized and ungraphitized carbons, the integral effect is not very sensitive to the difference between these samples. In the investigation [9] the value 300 ergs/sq. cm was found for the heat of wetting of an oxidized sample of the same Sferon-6 carbon; this value is more than double the value found by us and in the investigation [8]. It is probable that the value obtained in [9] in incorrect.

Theoretical Calculation of the Energy of Adsorption of Benzene on Graphite

It might be expected that the adsorption of benzene, like that of hexane, is due solely to dispersional interactions. We carried out a theoretical calculation of the energy of interaction of benzene with graphite by the same method as before [1]. The interaction energy of an isolated benzene molecule adsorbed on a plane having a graphite lattice was calculated from the equation:

$$\Phi = -C\left[\sum\left(\frac{1}{r^6} - \frac{r_0^6}{2r^{12}}\right) + \frac{\pi\nu}{6(r')^3}\right] = -Cf(r, r_0), \qquad (3)$$

in which C is the dispersional-interaction constant. The first term under the summation $\frac{1}{r^6}$ takes account of the energy of interaction between a CH of the benzene molecule and a carbon atom of the graphite lattice, placed at a distance r; the second term $\frac{r_0^6}{2r^{12}}$ takes account of the corresponding repulsion energy; r_0 is the equilibrium distance of the benzene molecule from the graphite surface, i. e., 3.55 A, the sum of the interplane distance in the graphite lattice (1.7 A) and the half-thickness of the benzene molecule (1.85 A) [10].

The summation was made for the 100 nearest atoms in the adsorbent. The last term of Equation 3 takes account of the interaction of the benzene molecule with all the remaining adsorbent atoms in accordance with London's integral formula [11] (ν is the number of carbon atoms in 1 cc and r' is 8.5 A); this last member forms only about 4% of the total value of $f(r, r_0)$.

The constant C was calculated from Kirkwood's equation [12]:

$$C = -6mc^2 \frac{\alpha\alpha_1}{\alpha/\chi + \alpha_1/\chi_1}, \qquad (4)$$

in which m is the mass of an electron, c is the velocity of light, and α and χ are the polarizabilities and diamagnetic susceptibilities of graphite and benzene, equal respectively to $0.937 \cdot 10^{-24}$ cc, $10.54 \cdot 10^{-30}$ cc; $10.32 \cdot 10^{-24}$ cc, $92.0 \cdot 10^{-30}$ cc. The value of $\sum\left(\frac{1}{r^6} - \frac{r_0^6}{2r^{12}}\right)$ depends on the position of the molecule over the graphite lattice. As the molecule is displaced it varies over a range of 15% [13]. As benzene molecules are mobile on a graphite surface at ordinary temperatures, we used the mean value of this summation in our calculations.

In the calculation of the interaction energy of benzene the value of $f(r, r_0)$ was found to be $3.20 \cdot 10^{65}$ cm^{-6}, which is considerably greater than the corresponding value for hexane, $2.86 \cdot 10^{65}$ cm^{-6} [1]. However, owing to the lower values of mean polarizability and diamagnetic susceptibility for benzene, the value of the constant C was found to be considerably less for benzene than for hexane, its value being $3.37 \cdot 10^{-65}$ kcal·cm^6/mole, which, for the energy of interaction between benzene and a graphite surface, gives $-\Phi = 10.8$ kcal/mole. For hexane $-\Phi = 12.0$ kcal/mole. The calculated value of $-\Phi$ for benzene agrees satisfactorily with the heat of adsorption that we found, namely 10.0 kcal/mole. In the investigation [1] we obtained 12.0 and 11.8 kcal/mole, respectively, for hexane. The change observed when we pass from the theoretical value for hexane to that for benzene is in close accord with the corresponding change in the experimental heats of adsorption.

As we pass from hexane to benzene, theoretical calculation shows a fall in adsorption energy from 12.0 to 10.8 kcal/mole, and experiment shows a fall in heat of adsorption from 11.8 to 10.0 kcal/mole.*

Hence, the heats of adsorption of these hydrocarbons on graphite are satisfactorily described theoretically by the energy of dispersional interaction with the graphite lattice.

The authors thank M. M. Dubinin for his interest and support in this work and A. P. Arkhipova for help in the measurements.

SUMMARY

1. With the aid of an automatic calorimeter having constant heat exchange and an adsorption apparatus with a capillary microburet, determinations were made of differential heats of adsorption and the adsorption isotherms for benzene vapor on carbon black, both graphitized and in its original oxidized state. Much of the surface of graphitized carbon is homogeneous and is filled at a constant heat of adsorption. The adsorption isotherm is satisfactorily described by the Langmuir and BET equations.

2. The relation of the free energy, total energy, and entropy of adsorption to the surface coverage was investigated. The respective standard values for adsorption of vapor and for wetting were determined.

3. A theoretical calculation of the adsorption energy of benzene was carried out by means of a summation of the dispersional interactions with the 100 nearest atoms of the graphite lattice, account being taken of interactions with the remaining atoms with the aid of an integral formula. The calculated value of the adsorption energy is very close to the measured heat of adsorption.

4. Comparisons are made between the isotherms and heats of adsorption of benzene and hexane vapors. As required by theoretical calculation, in the unimolecular region the heat of adsorption of benzene is considerably less than that of hexane.

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* For adsorption on silica gel the order is different: the heat of adsorption of benzene vapor is greater than that of hexane owing to the addition of the energy of the formation of π-complexes of benzene molecules with acidic hydroxyls of silicic acid [14].

** Russian Translation.

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HYDROGENATION OF CYCLOPENTADIENE IN BINARY MIXTURES WITH OTHER UNSATURATED HYDROCARBONS IN PRESENCE OF RANEY NICKEL

L. Kh. Freidlin and B. D. Polkovnikov

The selective hydrogenation of cyclic hydrocarbons having a system of conjugated double bonds in admixture with olefins has received little investigation. We recently [1] studied the hydrogenation of cyclopentadiene in presence of Raney nickel at 25°. The reaction proceeds in two stages: the cyclopentadiene is first hydrogenated as far as cyclopentene, after which the latter begins to combine with hydrogen with formation of cyclopentane. The rate of the process is greatly dependent on the nature of the solvent. In a methanol or ethanol medium both stages are rapid. In hydrocarbon solvents such as cyclohexane or benzene the second stage is slow and the stepwise character of the process is clearly evident on the kinetic curve. It may be supposed that the stepwise character of the hydrogenation of the unsaturated bonds of cyclopentadiene is to be attributed to adsorptional displacement, the cyclopentene formed being displaced by cyclopentadiene from the catalyst surface, whereas neither an alcohol nor cyclohexane can displace an olefin [2]. In this connection we have now studied the hydrogenation of cyclopentadiene in admixture with cyclopentene and other unsaturated hydrocarbons.

EXPERIMENTAL

Procedure. Experimental Conditions. The hydrogenation was carried out at 25° at ordinary pressure in a shaking glass hydrogenation flask (length 180 mm, diameter 30 mm), agitation being at a rate of 900 shakes per minute with a sweep of 12.7 cm. Special experiments showed that such agitation completely ensures reaction in the kinetic region. The solvents used were cyclohexane and 96% ethanol. For the reaction, freshly prepared cyclopentadiene (b.p. 41-42°, n_D^{20} 1.4442-1.4446) was used; it was prepared by depolymerization of the dimer. The olefins had the following constants: cyclopentene [fraction of b.p. 43.5-43.8° (756 mm); n_D^{20} 1.4252], cyclohexene [fraction of b.p. 82-83° (754 mm); n_D^{20} 1.4467], tolan [diphenylacetylene] [m.p. 60-61° (750 mm)], 1 octene [fraction of b.p. 121.2-122.6° (742 mm); n_D^{20} 1.4130].

The Raney nickel catalyst was prepared by leaching a 50% nickel-aluminum alloy with 20% sodium hydroxide solution for two hours at 100°. For each experiment a new portion (0.42 g) of the same sample of catalyst was taken. The hydrogen used was electrolytic and was freed from traces of oxygen.

In the experiments carried out in cyclohexane, the catalyst was washed from a spoon into the flask with 10 ml of ethanol, which was then poured off; the catalyst was then washed twice with cyclohexane (10 ml portions). Before the reaction the catalyst was saturated with hydrogen under the same conditions (temperature, solvent, rate of agitation) as those used for the hydrogenation. The sample of substance (or mixture of substances) to be hydrogenated was then introduced in 10 ml of cyclohexane and the hydrogenation was begun. All such operations were carried out in a stream of hydrogen. We estimated the rate of hydrogenation and the activity of the catalyst from the rate of absorption of hydrogen.

Hydrogenation of Cyclopentadiene in Binary Mixtures with Cyclopentene, Cyclohexene, 1-Octene, and Tolan. Figure 1 shows the kinetic curves for the hydrogenation of olefins in ethanol and in cyclohexane. It will be seen from Fig. 1 and Table 1 that, in an alcoholic medium, the compounds investigated are hydrogenated at a considerably higher rate than in cyclohexane. Thus, the half-period for the hydrogenation of a

sample of cyclopentene is 9 times as long, and of a sample of tolan is 16 times as long, in cyclohexane as in ethanol (Fig. 1, b and d). The half-period for the hydrogenation of 1-octene or cyclohexene in alcoholic solution is 3-5 minutes, but these compounds are hydrogenated very slowly in cyclohexane (Fig. 1, e and c).

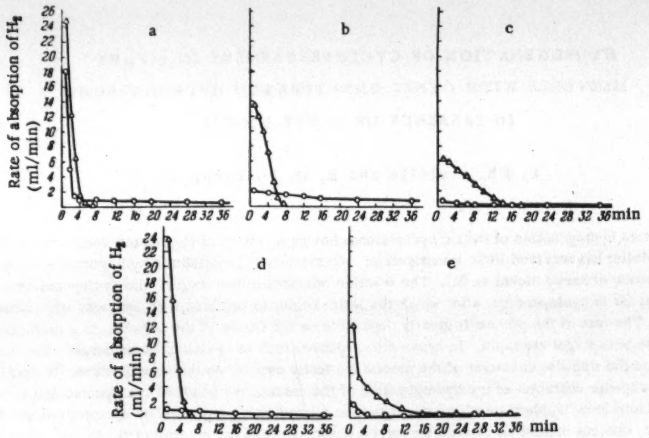

Fig. 1. Hydrogenation: a) cyclopentadiene; b) cyclopentene; c) cyclohexene; d) tolan; e) 1-octene. In ethanol (△) and in cyclohexane (○).

The same sort of difference is found when initial rates of hydrogenation are compared: in alcohol the rates for cyclohexene and tolan are respectively 12 and 19 times as high as in cyclohexane. The difference in the rates of hydrogenation of cyclopentadiene to cyclopentene in these solvents is not great (Fig. 1, a).

It will be seen from Fig. 2 that the kinetic curves for the hydrogenation of binary mixtures of cyclopentadiene with olefins in cyclohexane are, in general, repeats of the kinetic curve for the hydrogenation of cyclopentadiene alone in cyclohexane (Fig. 1, a). It may be supposed that in the hydrogenation of the mixture the steeply falling section of the curve again represents hydrogenation of cyclopentadiene to cyclopentene. The horizontal part of the curve represents the hydrogenation of cyclopentene and the second unsaturated component of the mixture. It is, in fact, found that the volume of hydrogen absorbed from the beginning of the reaction to the point of inflection on the kinetic curve is 24-25 ml on the average, which corresponds to 50% of the hydrogen necessary for the conversion of the cyclopentadiene into cyclopentane. Moreover, qualitative tests with hydroquinone in parallel experiments showed that at the time corresponding to the bend cyclopentadiene was absent from the mixture. This indicates the selectivity of the hydrogenation of cyclopentadiene (to cyclopentene) and confirms the correctness of our interpretation of the character of the kinetic curves of the hydrogenation of binary mixtures in cyclohexane. The character of the kinetic curves for the hydrogenation of binary mixtures in ethanol is such that it is impossible to infer that addition of hydrogen to the individual components of the mixture occurs in a stepwise manner (Fig. 2). It was shown by the hydroquinone reaction that, in alcoholic solution also, cyclopentadiene is absent from the solution after 50% of the hydrogen theoretically necessary for the conversion of cyclopentadiene into cyclopentane has been consumed.

In another series of experiments the second unsaturated component was at first hydrogenated in cyclohexane or alcohol and, after a few minutes, 0.00095 mole of cyclopentadiene was introduced into the flask in the appropriate solvent (5 ml) and hydrogenation was continued. It will be seen from Fig. 3 that, in both solvents, the rate of absorption of hydrogen rises sharply after the addition of cyclopentadiene. In ethanolic solution the

TABLE 1

Hydrogenation of Cyclopentadiene in Binary Mixtures with Cyclopentene, Cyclohexene, Tolan and 1-Octene in Ethanol and in Cyclohexane (Experimental conditions: weight of nickel 0.42 g; volume of solvent 10–15 ml; temperature 25°; rate of agitation 900 shakes per minute).

Substances hydrogenated	Hydrogenation in cyclohexane						Hydrogenation in ethanol				Qualitative reaction for cyclopentadiene at bend
	Wt. of olefin (g)	Initial rate of absorption of H_2 (ml/min)	Initial rate of absorp. of H_2 after addition of cyclopentadiene (ml/min)	Half-period of reaction (min)	H_2 consumed up to bend (ml)	Calculated consumption of H_2 (ml)	Wt. of olefin (g)	Initial rate of absorption of H_2 (ml/min)	Initial rate of absorp. of H_2 after addition of cyclopentadiene (ml/min)	Half-period of reaction (min)	
Cyclopentadiene	0.0620	18.0	—	3	24.4	24.5	0.0624	24.8	—	1	Negative
Cyclopentene	0.1290	2.1	—	18	—	24.0	0.1311	13.5	—	2	
Mixture of cyclopentadiene and cyclopentene	0.0651 0.1290	15.5	—	21	24.8	24.9 24.0	0.0626 0.1311	23.2	—	2.5	Negative
Cyclopentene, cyclopentadiene (added)	0.1327 0.0699	1.3	16.7	31	26.7**	24.8 26.8	0.1311 0.0626	14.8	23.5	3	—
Cyclohexene	0.1582	0.5	—	—	—	24.6	0.1557	6.3	—	5	—
Mixture of cyclopentadiene and cyclohexene	0.0614 0.1582	13.3	—	—	21.3	23.7 24.6	0.0624 0.1557	20.0	—	5	Negative
Cyclohexene, cyclopentadiene (added)	0.1582 0.0614	0.5	19.0	—	23.7**	23.8 23.6	0.1557 0.0624	7.4	21.6	6	—
Tolan	0.1692	1.2	—	16	—	24.8	0.1699	23.7	—	1	—
Mixture of cyclopentadiene and tolan	0.0620 0.1692	12.8	—	—	26.6	24.5 24.8	0.0624 0.1699	29.2	—	2	Negative
Tolan, cyclopentadiene (added)	0.1692 0.0620	0.6	14.9	—	25.1**	24.8 24.5	0.1699 0.0624	17.3	24.3	2.5	—
1-Octene	0.2080	1.6	—	—	—	23.8	0.2085	11.9	—	3.5	—
Mixture of cyclopentadiene and 1-octene	0.0623 0.2080	15.6	—	44	25.0	24.2 23.9	0.0612 0.2085	23.7	—	3.1	Negative
1-Octene, cyclopentadiene (added)	0.2080 0.0623	1.7	22.0	24	25.3**	23.9 24.3	0.2085 0.0612	9.9	24.8	8.6	—

* On the hydrogenation of cyclopentadiene to cyclopentene.

** Counted from the moment of introducing cyclopentadiene.

NOTE. The first of the figures bracketed together refers to the first component of the mixture and the second refers to the second component.

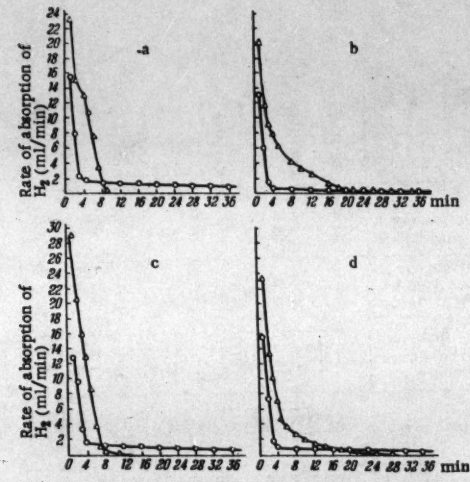

Fig. 2. Hydrogenation of binary mixtures of cyclopentadiene: a) with cyclopentene; b) with cyclohexene; c) with tolan; d) with 1-octene. In ethanol (△) and in cyclohexane (○).

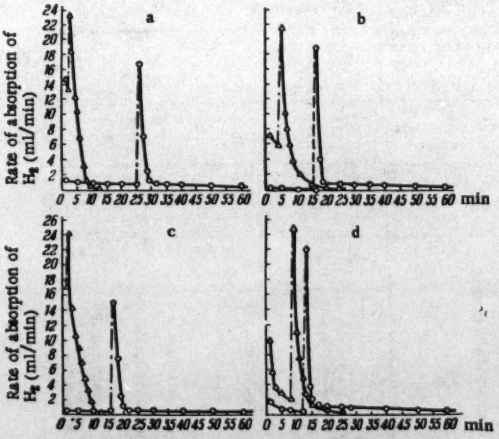

Fig. 3. Hydrogenation with addition of cyclopentadiene: a) cyclopentene; b) cyclohexene; c) tolan; d) 1-octene. In ethanol (△) and in cyclohexane (○).

TABLE 2

Hydrogenation of Cyclopentadiene in Binary Mixtures with Piperylene, 1-Heptyne, and Styrene in Cyclohexane

(Experimental conditions: weight of nickel 0.42 g; volume of cyclohexane 10-15 ml; temperature 25°; rate of agitation 900 shakes per minute)

Substances hydrogenated	Wt. of olefin (g)	Initial rate of absorption of H_2 (ml/min)	Initial rate of absorption of H_2 after addition of cyclopentadiene (ml/min)	Half-period of reaction min)	H_2 consumed up to bend (ml)	Calculated consumption of H_2 (ml)	Qualitative reaction for cyclopentadiene at bend
Cyclopentadiene	0.0627	17.8	—	3	23.3	48.8	Negative
Piperylene	0.0646	12.2	—	3	18.4	49.8	—
Mixture of Cyclopentadiene and piperylene	0.0628 0.0646	14.1	—	5	41.5	49.9 49.8	Positive
Piperylene, cyclopentadiene (added)	0.1305 0.0621	18.1	17.4	14	26.3*	98.4 48.3	—
Piperylene, cyclopentadiene (added)	0.1290 0.0621	20.2	16.1	16	38.4*	97.4 48.3	—
1-Heptyne	0.0874	5.4	—	8	—	46.5	—
Mixture of cyclopentadiene and 1-heptyne	0.0623 0.0874	11.8	—	6	—	48.2 46.5	Positive
1-Heptyne, cyclopentadiene (added)	0.0874 0.0623	6.9	18.1	9	24.8*	46.5 48.2	—
Styrene	0.2033	8.4	—	3.5	—	50.0	—
Mixture of cyclopentadiene and styrene	0.0627 0.2033	13.9	—	5.5	—	48.8 50.0	Positive
Styrene, cyclopentadiene (added)	0.2033 0.0627	11.0	17.7	4.6	30.1*	50.0 48.8	—

* Counted from moment of introducing cyclopentadiene.

initial rate of addition of hydrogen (maximum point on kinetic curve) after the introduction of cyclopentadiene greatly exceeds the initial rate of hydrogenation of the second unsaturated component of the mixture. In cyclohexane the initial rate of addition of hydrogen after the introduction of cyclopentadiene is close to the initial rate of hydrogenation of cyclopentadiene in this solvent. During hydrogenation in cyclohexane the consumption of hydrogen from the moment of introducing cyclopentadiene to the bend on the kinetic curve (about 25 ml) represents about 50% of the hydrogen necessary for the hydrogenation of cyclopentadiene to cyclopentane. Hence, from the moment at which cyclopentadiene is introduced into the reaction mixture hydrogenation of the second unsaturated hydrocarbon comes to a stop until the whole of the cyclopentadiene has been converted into cyclopentene.

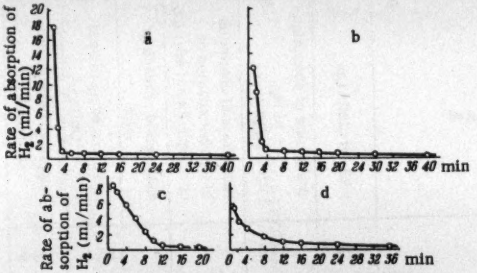

Fig. 4. Hydrogenation: a) cyclopentadiene; b) piperylene; c) styrene; d) heptyne.

The results show that, both in cyclohexane and in alcohol, cyclopentadiene displaces cyclopentene, cyclohexene, 1-octene, and tolan from the surface of a nickel catalyst. In the binary mixtures that we have studied, at first cyclopentadiene is selectively hydrogenated to cyclopentene, and only when this process is complete does hydrogen begin to add to other unsaturated hydrocarbons.

Hydrogenation of Cyclopentadiene in Binary Mixtures with Piperylene, 1-Heptyne and Styrene. The experimental conditions are shown in Table 2. Figure 4 gives the kinetic curves for the time-dependence of the rate of absorption of hydrogen in the hydrogenation of single unsaturated components; Figure 5 gives the curves for mixtures of these with cyclopentadiene in cyclohexane. It will be seen from Fig. 4 and Table 2 that, unlike the previously investigated unsaturated hydrocarbons (above), piperylene, styrene, and 1-heptyne are rapidly hydrogenated, even in a cyclohexane medium. The half-periods for complete hydrogenation of these compounds are 3, 3.5, and 8 minutes, respectively.

In its general features, the curve for the hydrogenation of piperylene (Fig. 4, b) repeats the curve for the hydrogenation of cyclopentadiene (Fig. 4, a). It also has a bend corresponding to the addition of about 50% of the hydrogen necessary for the complete saturation of the piperylene. The bend on the kinetic curve for the hydrogenation of 1-heptyne is less clearly marked. The rate of absorption of hydrogen in the hydrogenation of a mixture is less than the rate of addition of hydrogen to cyclopentadiene and greater than the rate of hydrogenation of the second component of the binary mixture taken.

The character of the kinetic curves for the hydrogenation of binary mixtures of cyclopentadiene with 1-heptyne (Fig. 5, c) and with styrene (Fig. 5, b) in cyclohexane does not enable us to infer that the addition of hydrogen to the individual components of the mixture proceeds in stepwise fashion. Experiments were, therefore, carried out in which test samples were taken at the moment when hydrogen had been consumed in an amount equivalent to that required to convert the cyclopentadiene present into cyclopentene and were tested for the presence of cyclopentadiene with hydroquinone. It was first established by special experiments that the other unsaturated hydrocarbons under investigation did not interfere in the detection of cyclopentadiene by this method. It was found that, at the stated moment of hydrogenation in cyclohexane, cyclopentadiene was still present in all three mixtures; in the mixtures with styrene, piperylene, and 1-heptyne it was detected after the consumption of 114.6, 134.2 and 135% of the hydrogen required for the conversion of cyclopentadiene into cyclopentene. These results show that, in binary mixtures, hydrogenation of cyclopentadiene is accompanied

by simultaneous hydrogenation of styrene, piperylene and 1-heptyne.

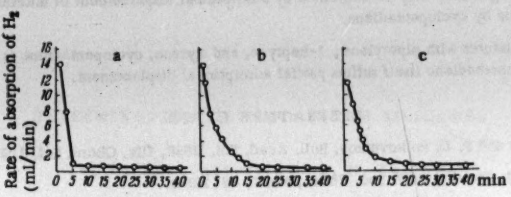

Fig. 5. Hydrogenation of binary mixtures of cyclopentadiene: a) with piperylene; b) with styrene; c) with 1-heptyne.

Figure 6 represents the results of experiments in which cyclopentadiene (0.00095 mole) was introduced into the flask 5-10 minutes after the beginning of the hydrogenation of the second component (styrene, piperylene, or 1-heptyne). These experiments were undertaken on the view that, if the unsaturated hydrocarbon of the binary mixture in cyclohexane was hydrogenated simultaneously with cyclopentadiene, then the consumption of hydrogen between the point of addition of cyclopentadiene and the bend should be appreciably higher

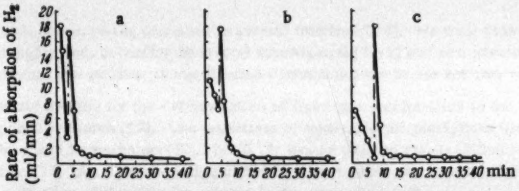

Fig. 6. Hydrogenation with addition of cyclopentadiene: a) piperylene; b) styrene; c) 1-heptyne.

than that which corresponds to the selective hydrogenation of cyclopentadiene alone (to cyclopentene).

It will be seen from Fig. 6 and Table 2 that the hydrogen consumption between the point of addition of cyclopentadiene and the bend is indeed appreciably higher than the amount necessary for the hydrogenation of cyclopentadiene to cyclopentene. In the experiment with 1-heptyne, cyclopentadiene was added after the consumption of about 50% of the hydrogen required to convert it into 1-heptene. In this case the consumption of hydrogen between the moment of introducing cyclopentadiene and the bend corresponds almost exactly to the amount necessary for the hydrogenation of cyclopentadiene to cyclopentene. Hence, in binary mixtures with piperylene, 1-heptyne, and styrene in a cyclohexane medium, cyclopentadiene is hydrogenated nonselectively in presence of Raney nickel.

SUMMARY

1. An investigation was made into the hydrogenation of cyclopentadiene in binary mixtures with other unsaturated hydrocarbons in presence of a Raney nickel catalyst.

2. It was shown that, in an alcohol medium, all the investigated unsaturated hydrocarbons combine with hydrogen considerably more rapidly than in a cyclohexane medium. Cyclohexene, cyclopentene, 1-octene, and tolan are hydrogenated particularly slowly in a hydrocarbon medium.

3. It was found that, both in alcohol and in cyclohexane, in mixtures of cyclopentadiene with cyclopentene, cyclohexene, 1-octene, and tolan, only the cyclopentadiene is hydrogenated at first (to cyclopentene); only when this process is complete does hydrogen begin to add to the second component of the binary mixture. This selectivity of hydrogenation may be explained by adsorptional displacement of unsaturated hydrocarbons from the catalyst surface by cyclopentadiene.

4. In its binary mixtures with piperylene, 1-heptyne, and styrene, cyclopentadiene is hydrogenated nonselectively, i. e., cyclopentadiene itself suffers partial adsorptional displacement.

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DETERMINATION OF FLUORINE IN SILICATES

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There is extensive literature on the determination of fluorine. We shall consider briefly the principal ways in which the problem of determining fluorine in silicates has been solved.

Fusion with sodium carbonate or other alkaline fusion agent is a widely used method for the digestion of the sample – it may, in fact, be the only method for silicates that are not decomposed by acids, irrespective of the analytical procedure selected for the final determination of fluorine. The melt is leached with water, and fluorine passes into solution in the form of sodium fluoride. The further treatment of the solution depends on the method selected for the determination of fluorine. The oldest method, which was developed by Berzelius [1] and by Rose [2] and was for a long time the only method for the determination of fluorine in silicates, requires a cycle of operations aiming at the complete removal of silicic acid and aluminum from alkaline and neutral solutions, fluorine then being isolated and weighed in the form of calcium fluoride.

The method is well known and is described in several treatises [3-6]. We must point out that the method is complicated and lengthy and, according to several investigators [7-11] and also according to our own observations, it gives somewhat low results; at low fluorine contents the results are not very reliable.

Another gravimetric method for the determination of fluorine – precipitation in the form of lead "fluorochloride" – was proposed by Starck [12]. The conditions of separating the precipitate were studied and more accurately defined by many investigators [10, 13-16]. It was established that lead fluorochloride is a compound of definite composition [17, 18]. Determination of the fluorine content can be carried out also by an indirect volumetric method – titration of the chlorine present in the precipitate [10].

Hoffmann and Lundell [9] proposed the use of this method for the determination of fluorine in silicates. They investigated the effect of silicic acid, aluminum, boron, alkali and ammonium salts, and other compounds on the completeness of the precipitation of lead fluorochloride. For the simultaneous determination of silica and fluorine it is recommended that silicic acid and aluminum be removed completely by precipitation with a zinc salt and ammoniacal zinc oxide. However, for the determination of fluorine only (without simultaneous determination of silica) the authors confine themselves to the separation of components interfering in the determination of fluorine by treatment with a solution of a zinc salt in sodium carbonate solution. This treatment does not ensure the complete removal of silicic acid and aluminum. Some variants of this procedure for the treatment of the solution before precipitation of lead fluorochloride do not generally require the separation of silicic acid and aluminum [10, 19]. These variants provide considerably simpler procedures for the determination of fluorine in silicates; it was important to determine the extent to which this simplification affects the accuracy of the estimation.

The determination of fluorine by separation in the form of PbFCl is applicable only when the fluorine content of the material to be analyzed is relatively high. Various variants of the indirect colorimetric determination of fluorine in silicates have been proposed for low fluorine contents. However the colorimetric determination of fluorine in silicates may be carried out, it is necessary to perform several preparatory operations, beginning generally with fusion of the silicate with sodium carbonate and aqueous extraction of the melt. It is recommended that interfering components should then be removed. For the separation of most of the silicic acid and aluminum the procedure proposed by Berzelius – treatment of the alkaline extract with ammonium carbonate – may be used. As applied to preparation of a sample for colorimetric determination of fluorine,

this method is described by Babko and Pilipenko [20]. One method for the colorimetric determination of fluorine is based on the change in the red color of the zirconium lake of alizarin in presence of fluorine. There are no references in the literature to the effect of the silicic acid remaining in the solution on the results of the colorimetric determination of fluorine with the aid of the zirconium lake of alizarin.

The various advantages of the colorimetric method of determining fluorine when the fluorine content is low prompted us to make a more detailed investigation of the conditions of applying this method to silicates.

A special group of methods is based on removal of fluorine by distillation in the form of volatile compounds – silicon tetrafluoride [21] and hydrofluosilicic acid [22]. The distillation method was first proposed for the determination of fluorine in fluorides; it is of limited application in the analysis of silicates, since most natural and synthetic silicates are not decomposed by acids or are decomposed incompletely. For silicates that are not decomposed by acids preliminary digestion with an alkaline fusion agent is necessary. In both cases colloidal silicic acid is bound to be formed when the solution is acidified. However, investigation of the elimination of the fluorine as hydrofluosilicic acid showed that the presence of a gel of silicic acid and alumina makes the elimination of fluorine incomplete [23-25].

For the determination of fluorine in silicates various methods have been proposed recently in which the silicate sample is prepared for analysis by fusion and separation of most of the silicic acid and aluminum before driving off the fluorine. This is attained either by fusion of the silicate with zinc oxide and sodium carbonate and leaching of the melt with water [25, 26] or fusion with sodium peroxide, dissolution of the melt in water and precipiatation of most of the silicic acid and aluminum with the aid of a zinc salt [27]. The authors consider that the precipitate contains a negligible amount of fluorine [25] or contains none at all [26, 27].

In the distillation method various methods for the determination of the fluorine in the distillate may be used; it is very usual to titrate the fluorine in the solution with thorium nitrate solution, as proposed by Willard and Winter [28] – the zirconium lake of alizarin is used as indicator, the titration being carried out in aqueous-alcoholic solution. Armstrong showed [29] that the presence of zirconium is not essential in titration with thorium nitrate, for the end point can be established also by the formation of the thorium lake of alizarin. The method has been investigated by several workers; particular attention has been paid to the question of the pH of the medium in which the titration is carried out [30-34].

In the present paper we give the results of experiments designed to define more closely the conditions for the colorimetric determination of low concentrations of fluorine in silicates with the aid of the zirconium lake of alizarin – and of large amounts of fluorine by the method of precipitation in the form of lead fluorochloride.

EXPERIMENTAL

Colorimetric Determination of Fluorine in Silicates with the aid of the Zirconium Lake of Alizarin

A weighed amount of the material is fused with four times this amount of a mixture of sodium and potassium carbonates, and the melt is leached with water [20]. Solid ammonium carbonate (2-4 g) is added, and the solution is heated and then evaporated on a water bath until the ammonium carbonate is completely decomposed. The precipitate contains most of the silicic acid and aluminum hydroxide; it is filtered off and washed with water. Fluorine is determined colorimetrically in an aliquot of the acidified filtrate with the aid of the zirconium lake of alizarin.

When ammonium carbonate is added, the pH of the sodium carbonate solution is lowered to 9-9.3. Under these conditions polymerization of silicic acid proceeds at an appreciable rate. With heating, the rate of polymerization increases and a gel of silicic acid finally separates. With further heating until the ammonium carbonate is completely decomposed, the pH of the solution rises somewhat and partial dissolution of the gel occurs; the amount of silicic acid remaining in the solution may therefore be considerable. Our experiments showed that for a 0.38 g sample of silica, the amount remaining in solution after separation of silicic acid by the method described is generally equivalent to 20-30 mg of silica.

The rate at which the color of the zirconium lake of alizarin changes in presence of fluorine increases with increase in the concentration of acid in the solution. It was shown that the maximum color is attained in one hour in 2 N HCl. The colorimetric determination was carried out on 50 ml of solution by the method of standard series. For low fluorine contents – 50γ – standards having a low content of the zirconia-alizarin lake

(5 ml) were used,* and for fluorine contents of greater than 50γ comparison was made with a series of standards having a higher content of the lake (10 ml). In the first series, the standards were at intervals of 5γ, and in the second series — 25γ.

Experiments were carried out with the object of determining the effect of the presence of silicic acid in the solution on the results of the colorimetric determination of fluorine in the solution. We took into account the fact that, as we had shown previously, the silicic acid content may attain 20-30 mg. Various amounts of standard silicic acid solution were introduced into 50 ml standard flasks, each containing 10 ml of sodium carbonate solution (0.6 g of sodium carbonate). The solution was neutralized with dilute hydrochloric acid (1 : 10), 8 ml of concentrated hydrochloric acid (sp. gr. 1.18) was added, and this was followed by 5 ml of the zirconia-alizarin solution. The solution was made up to the mark with distilled water, well mixed, and set aside for one hour. The change in color caused by the presence of silicic acid was compared with a series of standard solutions containing fluorine together with all the other reagents at the same concentrations. The experiments showed that, like fluorine, silicic acid breaks down the zirconia-alizarin lake, probably owing to

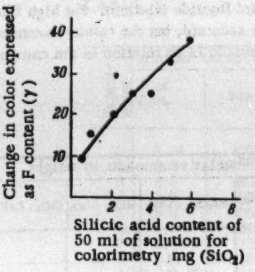

Fig. 1.

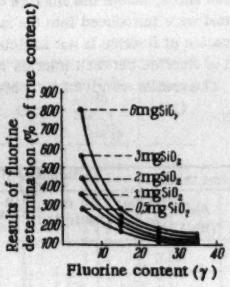

Fig. 2

the formation of zirconium silicates (Fig. 1). The change in color of the zirconia-alizarin lake in presence of silicic acid may result in high results for fluorine when silicic acid is incompletely removed; fluorine can, however, be determined colorimetrically.

Experiments on the determination of fluorine in solutions containing silicic acid gave the results shown in Fig. 2. When the fluorine content is 5γ, the change in the color of the zirconia-alizarin lake is almost equal to the sum of the effects of the fluorine and the silicic acid; with increase in the fluorine content, the observed color change is less than the summation value, but the amount of fluorine found (for an absolute content of up to 50γ) is nevertheless considerably greater than the actual amount. In the determination of fluorine, therefore, it is necessary to determine silicic acid colorimetrically in an aliquot of the solution and introduce the same amount of silicic acid into the standard solutions.

As already indicated, the determination of fluorine in silicates requires fusion of the sample with sodium carbonate and a series of operations for the removal of silicic acid and alumina. Many investigators [7-10] have shown that, for complete transfer of the fluorine to the aqueous extract of the alkali melt, it is necessary that the silica content of the material to be fused should be sufficiently high; in the analysis of materials poor in silica it is recommended that silica should be added during fusion. However, the relation of the completeness of leaching of fluorine to the contents of silica and alumina — the main components of the silicate — has not been completely determined.

* Preparation of a solution of the zirconia-alizarin lake: 0.87 g of zirconium nitrate is dissolved in 100 ml of water and 0.17 g of sodium alizarinsulfonate is dissolved in 100 ml of water; the zirconium nitrate solution is slowly added with shaking to the alizarinsulfonate solution, and the solution is set aside overnight. For the colorimetric determination the solution is diluted ten times with water.

In the cycle of operations for the removal of silicic acid and alumina, fluorine may be lost. This matter also is insufficiently clear. We carried out special experiments on these two questions: the results are given below.

The first series of experiments established the distribution of fluorine between solution and insoluble residue in the leaching of the melt $Na_2CO_3-CaF_2$ with water; the effect of the amount of sodium carbonate was determined. Calcium fluoride (200 mg) was fused with sodium carbonate, the melt was leached with hot water, and the insoluble residue was filtered off and washed with 0.5% sodium carbonate solution. The volume of the filtrate was made up to 250 ml with distilled water. Fluorine was determined colorimetrically in an aliquot of the solution.

The second series of experiments established the distribution of fluorine between solution and insoluble residue in the leaching of the melt $Na_2CO_3-CaF_2-SiO_2$; the effect of the amount of SiO_2 taken was determined. Special experiments were carried out to determine the distribution of fluorine between the solution and insoluble residue in the leaching of the melt $Na_2CO_3-CaF_2-SiO_2-Al_2O_3$. In these experiments the insoluble residue was further treated by boiling with 50 ml of 2% sodium carbonate solution. When the synthetic mixture contained silica, before the fluorine determination silicic acid was determined colorimetrically and the amounts found were introduced into the standard fluoride solutions. For high fluorine content the colorimetric determination of fluorine is not sufficiently accurate, but the results nevertheless give a clear picture of the distribution of fluorine between solution and residue in its relation to the composition of the material to be analyzed. The results are given in Table 1.

TABLE 1

Experiment	Amount taken				Amount of F Found (mg)		Relative amounts by weight		
	Na_2CO_3 (g)	SiO_2 (mg)	Al_2O_3 (mg)	F (mg) (as CaF_2)	in the solution	in the insoluble residue	$Na_2CO_3 : CaF_2$	$SiO_2 : Al_2O_3$	$SiO_2 : CaF_2$
1	1	—	—	97.4	58.2	39.5	5 : 1	—	—
2	4	—	—	97.4	82.7	16.5	20 : 1	—	—
3	6	—	—	97.4	88.8	9.2	30 : 1	—	—
4	4	—	—	97.4	94.1*	—	20 : 1	—	—
5	4	—	—	97.4	96.9**	—	20 : 1	—	—
6	4	100	—	97.4	98.0	—	—	—	1 : 2
7	4	50	—	97.4	98.0	—	—	—	1 : 4
8	4	30	—	97.4	98.0	—	—	—	1 : 6.7
9	4	10	—	97.4	93.8	—	—	—	1 : 20
10	4	10	—	97.4	98.0*	—	—	—	1 : 20
11	4	50	100	97.4	87.5	—	—	1 : 2	1 : 4
12	4	100	100	97.4	98.0	—	—	1 : 1	1 : 2
13	5	150	350	97.4	75.0	—	—	1 : 2.3	1 : 1.3
14	6	350	350	97.4	96.9	—	—	1 : 1	1 : 0.6
15	4	—	350	97.4	62.5	—	—	—	—

* The melt was leached with water, and the insoluble residue was treated for ten minutes at the boil with 50 ml of 2% sodium carbonate solution. Fluorine was determined in the combined filtrates.

** The insoluble residue was treated twice with 2% sodium carbonate solution under the same conditions.

In the fusion of calcium fluoride with sodium carbonate and the leaching of the melt with water, the equilibrium $CaF_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaF$ was established. As Experiments 1-3 showed, fusion even with a large excess of sodium carbonate (30 : 1) does not result in complete transfer of fluorine into the solution during the leaching of the melt. Increase in the completeness of the extraction of fluorine may be attained by repeated treatment of the insoluble residue with sodium carbonate solution (Experiments 4 and 5). It is known that

introduction of silica during fusion results in complete transfer of fluorine to the solution in the leaching of the melt; it is generally recommended that the weight of silica be 2.5-3 times that of calcium fluoride. Our results showed that the amount of silica can be considerably less: when the insoluble residue is given a supplementary treatment with sodium carbonate solution, a ratio of $SiO_2 : CaF_2$ of 1 : 20 by weight ensures complete passage of fluorine into solution. In presence of alumina, even a large excess of silica and supplementary treatment of the insoluble residue are insufficient to ensure complete transfer of fluorine to the solution (Experiments 11 and 13). As our results show, the amount of silica ensuring complete transfer of fluorine to the solution in the fusion of samples containing alumina is determined by the weight ratio $SiO_2 : Al_2O_3$. Almost complete transfer of fluorine to the solution is attained when the silica content is equal to or greater than the alumina content; the insoluble residue from the aqueous extraction must be treated with sodium carbonate solution (Experiments 12 and 14).

Special experiments were devoted to the study of the behavior of fluorine in the process of separating silicic acid and alumina by means of ammonium carbonate, the weight ratio $SiO_2 : Al_2O_3$ being varied in the material to be analyzed. The results are given in Table 2.

TABLE 2

Experiment	Amount taken (mg)			Weight ratio $SiO_2 : Al_2O_3$	F found (mg)
	F as CaF_2	SiO_2	Al_2O_3		
1	9.74	450	50	9 : 1	9.75
2	9.0	450	50	9 : 1	9.0
3	0.5	490	245	2 : 1	0.5
4	2.0	490	245	2 : 1	2.0
5	9.0	350	150	2 : 1	9.3
6	9.74	350	150	2 : 1	9.75
7	0.5	210	210	1 : 1	0.56
8	1.0	210	210	1 : 1	0.95
9	2.0	210	210	1 : 1	2.0
10	9.0	250	250	1 : 1	8.8
11	0.5	122	262	1 : 2	0.45
12	2.0	122	262	1 : 2	1.75
13	9.0	150	340	1 : 2	8.12
14	9.0	150	350	1 : 2	8.50
15	9.0	50	290	1 : 5,8	8.13
16	9.0	50	450	1 : 9	6.9
17	9.0	30	470	1 : 16	6.9
18	9.0	—	500	—	6.9

It will be seen from these results that the precipitates contain almost no fluorine when the silica content of the material to be analyzed is higher than the alumina content. For the inverse proportions, part of the fluorine is retained by the precipitate: the higher the alumina content, the worse the results. As the silica content of most natural silicate minerals and rocks is higher than the alumina content, addition of silica during fusion is unnecessary. Moreover, the high silicic acid content of the solution would complicate the colorimetric determination of fluorine.

Our proposed variant of the procedure for determining fluorine, in which silicic acid is first determined colorimetrically, enables us not only to determine the fluorine content more accurately, but also to determine the silica content simultaneously. Silica is determined by the usual methods in the precipitates, and to the silica content found is added the silica content of the solution, which is determined colorimetrically.

Determination of Fluorine by Precipitation as Lead Fluorochloride

In the separation of PbFCl, the solution must not contain aluminum. There are no direct references in the literature to the effect of silicic acid on the precipitation of lead fluorochloride: it is stated only that, in the volumetric method, small amounts of silica have no effect, but the precipitate is difficult to filter when the silica content is higher than 50 mg.

Experiments on synthetic solutions enabled us to reach the following conclusions: 1) presence of silicic acid retards the separation of the lead fluorochloride precipitate, and at a silica content of more than 50 mg complete separation is not attained even after 15 hours of settling; 2) presence of alumina in an amount of 3-4 mg results in the nonprecipitation of about 1 mg of fluorine.

Experiment showed, therefore, that the solution prepared for the precipitation of lead fluorochloride must be free from aluminum, whereas silicic acid may be present in an amount not exceeding 50 mg of SiO_2. By Berzelius's method, complete removal of alumina and silicic acid is attained by two precipitations from the solution obtained by leaching the alkali melt. The first precipitation of the bulk of the silicic acid and alumina is effected by means of ammonium carbonate from a sodium carbonate solution, and the second is effected by means of ammoniacal zinc oxide. When the fluorine content is high, it is recommended that it should be further extracted from all the precipitates separated.

With the object of shortening the operation of preparing the solution, we carried out experiments on the separation of the alumina and the bulk of the silicic acid with the aid of ammonium carbonate from an alkaline extract of the melt, which was first neutralized to Methyl orange with nitric acid. The filtrate was investigated for completeness of separation of alumina: in all experiments 6-8 mg of aluminum was found in it. It must be pointed out that, in the preparation of the solution in the way recommended by Berzelius, and also by Hoffmann and Lundell, complete separation of the aluminum is again not attained. Thus, in the analysis of a mixture of aluminosilicates and calcium fluoride (present in large amount), the aluminum content of the solution was 3-4 mg of Al_2O_3.

In other experiments on material of high fluorine content we investigated the distribution of fluorine between solution and precipitate, the latter being formed by the above-described simplified method. Fluorine was determined in the solution by precipitation of lead fluorochloride; an aliquot of the solution was taken, the volume being chosen so that the aluminum content was not greater than 3 mg of Al_2O_3. As indicated above, such an aluminum content is associated with some incompleteness of precipitation of fluorine, but when the total content is high the error is relatively small. Fluorine was determined in the combined precipitates by the colorimetric method. The results of these experiments are give in Table 3.

TABLE 3

Experiment	Amount taken (mg)			Amount found (mg)			Error of determination (mg)
	SiO_2	Al_2O_3	F as CaF_2	in soln. (volumetric)	in ppts. (colorimetric)	total	
1	250	250	97.4	20.9	—	—	—
2	650	350	97.4	76.5	—	—	—
3	350	150	97.4	90.7	6.1	96.8	—0.6
				91.2	6.1	97.3	—0.1
4	437	190	97.4	88.6	7.35	95.95	1.45
				89.8	6.1	95.90	—1.5
5	437	190	24.35	20.0	3.7	23.7	—0.65
				20.8	3.06	23.86	—0.5
6	750	250	97.4	89.0	7.35	96.35	—1.05
				89.0	7.35	96.35	
7	570	190	97.4	88.6	7.35	95.95	—1.45
				86.0	9.2	95.2	—2.2
8	570	190	48.7	37.6	8.7	46.3	—2.4
				39.07	7.35	46.42	—2.28
9	500	160	97.4	89.4	7.35	96.75	—0.65
				88.2	8.2	96.4	—1.0
10	1150	350	97.4	89.4	7.5	96.9	—0.5
				89.4	7.5	96.9	—0.5

As will be seen from the data in Table 3, in the rapid variant for the preparation of the solution which we have proposed, the precipitates entrain more fluorine than under the generally recommended conditions. The entrainment of fluorine by the precipitates diminishes as the weight ratio $SiO_2:Al_2O_3$ increases. When this ratio becomes greater than 2:1, the amount of fluorine entrained by the precipitate becomes constant and does not change substantially with further increase in the silica content.

The fluorine content of the precipitates lies within the limits within which colorimetric determination is possible. The total content of fluorine, as established by volumetric determination (PbFCl) in the solution and by colorimetric determination in the precipitates, can be regarded as sufficiently accurate at high fluorine contents. The results are somewhat low, which can be readily explained by slight incompleteness of the precipitation of lead fluorochloride owing to incomplete separation of alumina. We consider that the proposed simplified variant of the procedure, which considerably reduces the time required for the analysis, can be recommended for the routine analysis of silicate materials rich in fluorides.

SUMMARY

1. It was shown that silicic acid interferes in the colorimetric determination of fluorine by the zirconia-alizarin method by combining with zirconium and reducing the red component of the color. In order to avoid error it is proposed to determine silicic acid colorimetrically in an aliquot of the solution and introduce the amount so found into the standard fluoride solutions.

2. A study was made of the conditions under which fluorine passes into solution in the process of fusing the material with sodium carbonate and then leaching the melt with water. It was shown that, in absence of silica and alumina in the material to be analyzed (e. g., CaF_2), complete extraction of fluorine can be attained by addition of a very small amount of silica — very much less than is usually recommended.

3. The conditions for the separation of fluorine in the form of lead fluorochloride were investigated. It was shown that the separation of the precipitate is retarded by the presence of silicic acid in the solution, and the precipitation of fluorine is incomplete when the silica content is high.

4. A variant of the procedure for the determination of high fluorine contents in silicate materials is proposed: the preparation of the solution is simplified, and fluorine is determined as the sum of the amount found volumetrically in the solution and the amount found colorimetrically in the precipitates.

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PHYSICAL BASIS OF THE REACTIVITY OF CARBONYL COMPOUNDS

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1. Butlerov, as also Markovnikov, imagined a molecule as an actually existing dynamic spatial system of atoms which are in constant motion and are bound together by affinity forces. According to the ideas of Butlerov and Markovnikov, in a molecule, "we always have a certain state of dynamic equilibrium" [1] established as a result of "the combined effects of all the chemical and physical influences" [2], which, in principle, cannot be isolated from one another. However, Butlerov and Markovnikov saw that the physics of that time was not sufficiently advanced to participate with chemistry in the development of a unified physicochemical theory of the structure and reactivity of a molecule; they regarded this as a problem of "the future dynamic theory of chemistry" [3]. With regard to the chemical theory of their time they wrote that, in its creation and development, " we may as yet discuss only chemical effects, as being best known to us" [4]. Being compelled to accept this temporary isolation of the chemical aspect of his theory from the physical aspect, Butlerov, in the creation and development of this theory, consciously tried to reflect this fact even in his terminology [5]; he spoke of the theory of chemical structure, having as its object the establishment of "the distribution of the chemical bond between atoms" [6] and the determination of "the order of a chemical bond existing between atoms in a 'particle' " [7] and its representation in a single structural formula for a given molecule under given conditions [8], and so on.

In physics, great advances have now been made in our knowledge of the structure of the individual molecule as a dynamic spatial system of interacting atoms which is in a definite state of dynamic equilibrium under given conditions. However, the development (particularly during the twenties and thirties) of the physicochemical theory of the structure and reactivity of a molecule — which has proceeded in various directions associated in various degrees with sound theoretical and experimental foundations — is still far from attaining a generally recognized state of finality as regards the basic underlying principles. This position is partly attributable to substantial experimental difficulties, which still exist, in the detailed examination of an individual molecule with all the specific characteristics of the physical states of the individual bonds.

Actually, experimental determinations of quantitites of such great importance for the theory as dipole moment (polarity), polarizability (displaceability of the electronic envelope), and others refer to the molecule as a whole, and not to its individual bonds. Such important quantitites as bond energy and interatomic distances, especially for bonds containing a hydrogen atom, have been determined insufficiently accurately for the purpose of the theory and generally for conditions removed from the specific conditions in individual molecules; the values obtained have then been assigned to bonds of the same sort (e. g., C—H) in molecules that vary greatly in composition and structure.

This substantial gap in our knowledge of the individual molecule forces the theorist to have recourse to hypothetic assumptions and calculations regarding the polarity of individual bonds in a given individual molecule, the character and degree of their polarizability in the form of various "mechanisms" of electron displacement, the variation in the electron density of bonds,* bond energies, interatomic distances, etc., and moreover,

* The distribution of electron density in a molecule may be extremely nonuniform; for example, in a shortened (under the influence of neighboring atoms and other structural factors) C—H bond, the binding electrons of the outer electron shells of these atoms, which are in constant orbital motion, carry out their motions in a smaller volume and have a higher effective density than in a lengthened C—H bond, etc.

these suppositions are often arbitrary and without experimental foundation.

There naturally arises a question of great importance: from the arsenal of experimentally determined physical parameters of a molecule to select those which can directly characterize with adequate accuracy the specific physical state of individual bonds in the individual molecule as a dynamic self-equilibrating spatial nucleus-electron system; for it is just this sort of experimental data that is now necessary for the further development of the theory of structure and the understanding of the principles underlying the reactivities of individual substances.

Taking a clear example, in which we shall make comparisons of relevant physical and chemical data for a given bond, we shall first show the dependence of the chemical nature of this bond on its physical condition as expressed by experimentally determined parameters.

2. One of the clearest examples of the manifestation of physical, and the associated chemical, interaction between atoms in a molecule is found in the great variation in the chemical and physical nature of a hydrogen atom according as it occurs in a hydroxyl such as is found in a strong acid, e. g., oxalic acid, or in a hydroxyl such as the OH^- ion. In the first case the interatomic distance $\underline{r}$ in the O—H bond is much greater than normal, the proton of the hydrogen atom being almost freed from the dynamic orbital-electron system of the hydroxyl, i.e., the hydrogen atom is almost completely "protonized." In this sense we may speak also of the protonization of the O—H bond as a particular case of very marked polarity of a bond containing a hydrogen atom. The electron density of such a bond is greatly reduced.* The initiation of various reactions in which the hydroxyl group participates arises, in the case under examination, mainly from this protonized or almost protonized hydrogen atom $(R\dot{\ddot{O}}\dot{x})\overset{\cdot\cdot}{\rceil}H^+$. Furthermore, for such a hydroxyl, the bond energy E and the vibrational frequency ν are much below normal. In the second case, on the other hand, the interatomic distance $\underline{r}$ is much less than normal: the proton of the hydrogen atom is, as it were, deeply drawn into the dynamic electron system of the hydroxyl ion $(\dot{x}\ \ddot{O}H\dot{x})^-$, the electron orbits overlap greatly. In this sense we may speak of the electronization of the O—H bond; in the given case this bond has enhanced electron density. The initiation of various reactions with the hydroxyl now arises mainly from electrons of the outer electron shell of the hydroxyl ion. Also, the bond energy E and the vibrational frequency ν of such a hydroxyl are much higher than normal.

The concept of the protonization of a bond, as is not difficult to see, is one of the limiting cases of its electronization when this is greatly depressed in bonds of the type X—H (X = O, F, etc).

The range of variation of the above-mentioned three physical parameters of the hydroxyl group is very considerable, particularly for ν and E (Table 1) [9].

TABLE 1

Vibrational Frequencies ν, Bond Energies E, and Interatomic Distances $\underline{r}$ for the Hydroxyl Groups of Various Compounds.

Compound	ν (cm^{-1})	E (kcal/mole)	r (A)
Oxalic acid (β form, crystalline)	2500	51	1.147
OH radical	3480	100	0.971
Methanol (gas)	3683	112	0.960
OH^- ion	4200	145	0.906

* With regard to this concept see the preceding footnote.

As will be seen, a definite change in the chemical nature of the O—H bond from strongly acidic (RO^-H^+) to strongly ionic (OH^-) stands in strict relationship with change in its physical state, as characterized by the three selected physical parameters; the directions of the changes correspond strictly. This correlation in the directions of changes in ν, E, and r for bonds having characteristic frequencies (O—H, C—H, etc.) is confirmed without exception by extensive experimental material. In this connection it should be noted that, as the range of change of vibrational frequencies is greater than for the other two parameters and as vibrational frequencies can be more readily and accurately determined experimentally (optically) than bond energies and interatomic distances, for bonds having characteristic vibrational frequencies (it is essential not to lose sight of this condition) the direction and magnitude of changes in all three parameters can be assessed from the direction and magnitude of the change in vibrational frequency.

From this discussion it will be seen that the parameters ν, E, and r must not be regarded as being primary physical factors determining the chemical nature of a molecule and its reactivity. The primary physical factors are electron-neucleus interactions in the molecule, as a nucleus-electron system in a state of dynamic equilibrium. It is this interaction that is suitably expressed and manifested in our selected bond parameters — mechanical ν, energetic E, and geometric r — so that by the strictly interrelated changes in these parameters in characteristic bonds we may form an idea of the physical state of the latter — of the electron-nucleus interaction in them, of change in their electron density,* etc. The concept of the electronization of a characteristic bond determined through its parameters ν, E, r in their strict interrelationship is an exact characterization, far-reaching in its concreteness, of the physical state of a bond as an element of a dynamic self-equilibrating nucleus-electron system; moreover, in this way it is possible to learn fine details concerning the physical state of individual bonds,** which are generally inaccessible*** for other methods.

3. We have now discussed the interrelationship between the physical parameters ν, E, and r and the chemical nature of the O—H bond. However, if the partner of hydrogen in the bond is an atom other than oxygen, then the phenomena of protonization and electronization may proceed somewhat differently.

Owing to the extremely high Gordy electronegativity of the oxygen atom (3.45) as compared with that of the hydrogen atom (2.13), in no known compound does the oxygen atom give electrons to the hydrogen atom under normal conditions, i. e., no compounds are known in which the limiting distribution of electrons in the O—H bond is of the form RO^+/H^-. Owing to this relationship of electronegativities, the oxygen atom, in drawing the dynamic orbital-electron system of the hydroxyl bond to itself, either in some measure frees the hydrogen atom from the system as a proton (since the latter together with electrons cannot approach closely to an oxygen atom owing to the repulsive forces that arise and rapidly increase at short interatomic distances), or, in another type of compounds, separates from the residue of the molecule together with a hydrogen atom in the form of an OH radical or OH^- ion.

In compounds in which hydrogen is attached to other atoms, the range of variation of the parameters of the X—H bonds (X = C, N, halogen, etc.) in the direction of the protonization or electronization of the hydrogen atom is substantially different from that found in the O—H bond. The extreme limits of the dynamic change in the orbital-electron system may be different. In the C—H bond, for example, this range is considerably narrower than in the O—H bond. Under the usual conditions we are not concerned with the formation of the $(CH)^-$ ion in RCH (R is the residue of the molecule) because of the smaller difference between the electronegativities of C (2.55) and H (2.13), as compared with the difference between O (3.43) and H (2.13), and also the firmness of the binding of the C atom to the residue of the molecule by three valencies, and not one as in the

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* See Preceding footnotes.

** For example: data on symmetrical and antisymmetrical vibrations of C—H bonds. A relevant matter in this connection is the question of the correlation between the limits of electronization of a bond and its physical nature; we shall not discuss this in detail in this paper.

*** For example: for the topographical aspect of the determination of electron density in the x-ray structure analysis of crystals by the Fourier method, which is limited in scope and can provide comparatively little information on the properties of individual characteristic bonds of the X—H type (X = C, O, etc.) and on their reactivity in individual molecules.

case of the oxygen of the hydroxyl group, etc. In the C—H and Si—H bonds (owing to the fact that the electronegativity of the carbon atom is only slightly greater than that of the hydrogen atom, and the electronegativity of the silicon atom (1.8) is even less than that of carbon), no "creeping" of the electron shell from the hydrogen atom, due to the effect of neighboring strongly electronegative atoms in themolecule, etc., occurs; it is attracted together with the proton, and this occurs all the more because the "reserves" of interatomic distance (unlike those in O—H and F—H bonds, which are greatly shortened) are considerable in C—H and Si—H bonds, i. e., repulsive forces do not hinder the attraction of the proton.

An illuminating example is to be found in the growing protonization of the O—H bond and growing electronization of the C—H bonds in the series acetic, monochloroacetic, dichloroacetic and trichloroacetic acids. As is well known, in this series the acid dissociation constant of the O—H bond increases sharply (i. e., the vibrational frequency and bond energy fall, and the interatomic distance increases); on the other hand, the C—H bond is electronized, as indicated by rise in vibrational frequency (and consequently rise in bond energy and reduction in the interatomic distance) (Table 2 [10]).

TABLE 2

Vibrational Frequencies of Acetic and Chloroacetic Acids and Other Compounds (cm^{-1})

C—H of CH_3				C—H of CH_2			Methylidyne C—H	
Compound	ν			Compound	ν		Compound	ν
CH_3—COOH	2900s*	2941a**	2990a	CH_2Cl—COOH	2960	3002a	$CHCl_3$—COOH	3018
CH_3 of n-paraffins	2879s	2938a	2967a	CH_2 of n-paraffins	2853	2908a	Methylidyne of hydrocarbons	2870
Rise	+21	+3	+23	Rise	+107	+94	Rise	+148

* s— symmetrical vibration; ** a— antisymmetrical vibration.

4. It is natural to extend the concept of greater or lesser electronization — determined by the relative values of the parameters ν, E, and r as characterized above — to the characteristic bond C = O, as also the multiple CC bonds, etc. Increase in the electronization of these bonds is expressed, as in OH, CH and other bonds, in rise in vibrational frequencies and energies, and reduction in interatomic distances; reduction in electronization is expressed in the opposite changes in these parameters, as will be seen from Tables 3 and 4.

TABLE 3

Parameters ν, E, and r in Single and Multiple CC Bonds

Bond	Compound	ν (cm^{-1}) [10a]	E* (kcal/mole [11])	r (A)
C—C	C_2H_6	992	83	1.543
C=C	C_2H_4	1621	110	1.353
C≡C	C_2H_2	1974	145	1.207

* The heat of sublimation of carbon is taken as 138 kcal/mole [11].

Although change in the multiplicity of the bond causes a sudden change in the state of electronization of the bond and its neighbors (see Tables 3 and 4), the mutual effects of atoms in the molecule smooth out these sudden transitions in the sense that, as a result of these interactions, a double bond may, in its parameters, pass

through all intermediate stages and approach the region of the triple bond; in the course of these changes the chemical nature of the bond changes correspondingly.

All the above discussion indicates that the concept of the electronization of a bond, determined through the parameters ν, E, and $\underline{r}$, permits experimental investigation of electron-nucleus interactions occurring in characteristic bonds and changes of electron density in these bonds due to mutual effects of atoms in the molecule and the structure of the molecule, etc., and it thus enables us to reveal experimentally the physical states in which the molecule reacts in various reactions, showing various reactivities; it enables us to determine whether various hypotheses regarding the displacements of electrons in bonds are in accordance with actuality.

There are two points that we wish to emphasize: 1) increase in bond energy due to increased electronization of the bond implies strengthening of the bond against rupture, but it may be accompanied (on attainment of a certain limit of electronization) by increased reactivity of atoms of this bond, i.e., by chemical instability; 2) it is, of course, impossible to consider the phenomena of electronization and protonization of bonds as factors in reactivity divorced from other factors (chemical structure of other reactants, geometry of the molecule, reaction conditions, etc.), but only in their mutual relationship with these factors.

TABLE 4

Parameters ν, E, and $\underline{r}$ of C = O Bonds in Various Compounds

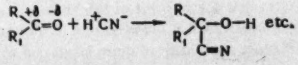
No.	Substance	Formula	ν (cm^{-1}) [12]	E (kcal/mole) [13]	r (A) [13]
I	Carbon monoxide (for comparison)	CO*	2155	211	1,128
II 1	Ketene	$H_2C{=}C{=}O$	2049	(206)	1.17
II 2	Phosgene	$Cl_2C{=}O$	1808	(192)	1.18
II 3	Formaldehyde	$H_2C{=}O$	1744	190	1.21
II 4	Acetaldehyde	CH_3-CHO	1720	184	1.22
II 5	Acetone	$CH_3-CO-CH_3$	1707	(183)	—
II 6	Oxoctenol***	$(H_3C)_3C-C(=O)-CH(-O-H)-C(CH_3)_3$	1692	(182)	—
II 7	Acetic acid (dimer)	$H_3CC(=O)-O\cdots H-O-C(=O)CH_3$	1668	(180)	1.25
III	C–O bond in CH_3-OH (for comparison)	CH_3-OH	1033	86.5	1.44

* Langmuir, Herzberg and other authors speak of an approach to a triple bond in carbon monoxide [14, 15].

** The heat of sublimation of carbon is taken as 190 kcal/mole [13]. The figures in parentheses are estimates made from the curve for the relation of vibration frequency to bond energy.

*** 4-Hydroxy-2,2,4-trimethyl-3-pentanone.

5. The hypothesis of electron displacement in a carbonyl group as the physical basis of the reactivity of the group in carbonyl compounds [16] is very widely adopted at present: "Addition reactions in this group of substances are controlled by the electron shift $C\overset{\curvearrowright}{=}O$, and the displacement determines the orientation of the adding molecule unequivocally," for example, [17]:



Such a displacement of electrons in a carbonyl group is explained in two ways on a hypothetical basis: 1) on the basis of the hypothesis of a possible inductional shift of valency electrons in the C = O bonds in the direction of the oxygen atom because of its higher positive charge (+6), as compared with the charge of the carbon atom (+4), i.e., on the basis of the hypothesis of the existence of a —I effect on the oxygen atom [18]; 2) on the hypothesis of the presence of a tautomeric effect —T in the carbonyl group, i.e., a tendency for the doubly bonded oxygen atom to reduce its valence, a process which, if it went to completion, would result in the formation of a semipolar bond $\overset{+}{C}—\overline{O}$ in the carbonyl group [19].*

Even the authors of this hypothesis speak of the inseparability of the actions of these two supposed effects in the carbonyl group [21], confining themselves to a graphical representation of the electron shift in the C = O bond in the form $>C\overset{\frown}{=}O$, $>\overset{+\delta}{C}—\overset{-\delta}{O}$, $>\overset{+}{C}—\overline{O}$ etc. and referring to partial polarization of the C = O group [22] and so on. The authors of the hypothesis do not cite any direct physical experiment in support of the described hypothetical electron shift in the carbonyl group (by the —I or —T mechanism); until quite recently they have regarded the physical side of the matter on a purely hypothetical plane.

However, in the light of our discussion above, direct verification of the hypothesis is quite possible, and we shall now discuss this question.

6. According to the hypothesis under examination, the oxygen atom of a carbonyl group to a certain extent plays the same part in relation to the carbon atom as it plays in the hydroxyl group in relation to the hydrogen atom, i.e., it again draws electrons from its partner along the bond and makes this partner (C) in some degree positive. The characteristic bond C = O, being on this hypothesis more polar on account of the —I effect (or less covalent on account of the —T effect) than is indiciated by its simple classical formula with two valence lines, must naturally have substantially different dynamic characteristics, expressed by the parameters ν, E, and r from those which it would possess if it remained a simple double bond C = O; i.e., its interatomic distance should be greater, its bond energy and vibrational frequency lower, and its electron density greatly reduced. The double bond, therefore, should be characterized by lower ν and E and greater r (i.e., should be less electronized and have a lower electron density) in $\begin{matrix}H\\H\end{matrix}\!\!>\!C=O$, for example, as compared with $\begin{matrix}H\\H\end{matrix}\!\!>\!C=CH_2$ (the bonds C—H, C = C, and C = O are characteristic); moreover, this should be so not only because of the supposed lowering of the double-bond character in C = O, as compared with C = C (in which there is no basis for such lowering to occur, owing to the symmetry of charges), but also because of the greater mass of the oxygen atom as compared with the mass of the carbon atom. However, in spite of this last fact, the actual picture observed is quite the opposite to that portrayed above:**

	ν(cm^{-1})	E(kcal/mole)	r (A)
$H_2C=CH_2$	1621	110	1.353
$H_2C=O$	1744	149	1.210

* Whereas, according to this hypothesis, the induction effect —I represents a state of permanent electronic strain (an electronic shift), the tautomeric effect —T, when taken to completion, represents the transfer of an electron pair from the C-octet to the O-octet [20].

** See Tables 3 and 4. In the determination of E, the heat of sublimation of carbon was taken to be 138 kcal/mole [11] in both cases. We do not cite the other numerous examples that indicate that, as compared with the C=C bond, the C=O bond is characterized by higher ν and E and lower r.

The rise in μ and E for C = O, as compared with C = C, is very great, as also is the shortening of the interatomic distance: the latter is 11%, i.e., considerably higher (by about 2%) than would have been expected if account were taken only of the somewhat smaller covalent radius of the O atom as compared with that of the carbon atom in single bonds.

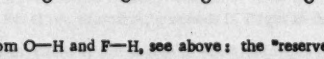
These data quite unequivocally indicate that a hypothetical shift of the type $\overset{+}{C}-\overset{-}{O}.\ C=\overset{+\delta}{O}.\ C=\overset{-\delta}{O}$, etc., does not take place in the carbonyl group. The electron-nucleus interactions in the C = O bond resemble not those observed in the O—H bond, but rather those occurring in the C—H bond: under the influence of the difference in electronegativities, the oxygen atom of the carbonyl group does not draw electrons from the C atom (as if by the action of the −I and −T effects of the hypothesis discussed above). In the struggle between C and O for binding electrons there is a compacting of the whole carbonyl bond — the nuclei approach one another and the electron density and electronization of the bond increase. This is possible 1) because of the "reserves" of interatomic distance in the C = O bond of carbonyl compounds* (this can be seen by a comparison with the interatomic distance in carbon monoxide,** see Table 4); 2) because of the inadequate, even though considerable, difference in the electronegativities of C and O; and for other reasons.

Actually, the relative electronegativities of the atoms are:

$$\frac{O}{K} = 4.37; \quad \frac{O}{H} = 1.64; \quad \frac{O}{C} = 1.37; \quad \frac{C}{H} = 1.20.$$

With such ratios of electronegativities, the drawing of the electron shell from the K atom in K^+OH^- is quite understandable. But already in the alcohols the drawing of the electron shell from the hydrogen atom proceeds to an insignificant extent: the acid dissociation constants of alcohols are very small. As is well known, this constant increases greatly in chloro acetic acids, in which the otherwise inadequate ratio of electronegativities $\frac{O}{H} = 1.64$ is increased by a supplementary factor corresponding to the effect of a chlorine atom, which is observed in concrete form in the sharp increase in dissociation constant as we pass from acetic acid to mono-, di-, and trichloroacetic acids. The still lower electronegativity ratio $\frac{O}{C} = 1.37$ in association with the above-mentioned "reserve" in interatomic distance leads not to drawing of electrons from the C atom, but, as in the case of the C—H bond, to compacting of the bond owing to the mutual approach of the nuclei and increase in electron density with, of course, the formation of a certain asymmetry of distribution of the electron density between the C and O atoms (this will arise if only from the fact that the electron shell of the oxygen atom is considerably larger than that of the carbon atom; the electron shell of the oxygen atom, unlike that of the carbon atom, contains electrons that are not concerned in interatomic bonds).

7. We will turn to an examination of the second thesis of the hypothesis under examination. According to this, allegedly owing to the positive character of the carbon atom of the carbonyl group, "the power to add to a carbonyl group is generally possessed only by nucleophilic reagents" [16] and this power is lost together, it is suggested, with reduction in the positive character of the carbon atom of the carbonyl group, when there are corresponding electron shifts in neighboring C—X (X = H, Cl, etc.), as for example, in the series [23]:



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* As in C—H, as distinct from O—H and F—H, see above: the "reserves" in interatomic distance in the C = O bond do not allow any sharp rise in the repulsive forces to occur.

** The CO molecule is included in Table 4 for comparison. We must point out that the reason for the association of high electronization with a fair degree of chemical inertness in the CO molecule (as in the isoelectronic molecule N_2) must be sought in the similarity of its outer electron shell to the octet of an inert gas; this matter was elucidated by Langmuir [14].

This so-called +T effect is alleged to polarize the C—Cl bond in the direction $\overset{-\delta}{C}-\overset{+\delta}{Cl}$, to protonize the hydrogens of the methyl group, and to produce a sesquipolar bond in the CO of the carboxyl ion. In other words, owing to the donating of electrons by X atoms in the direction of the carbonyl C, the bonds C—Cl and C—H_3 must in some measure become polar and, like C=O, must have lower electron density and lower electronization (owing to −I or −T effects); their dynamic characterization must be marked by lower ν and E and greater r. However, exact experimental data indicate the opposite, as will be seen from Tables 2 and 5 [10]: mutual approach of nuclei and increase in electron density occur, i.e., increased electronization takes place in these bonds. This is unequivocally indicated by the enhanced level of the vibrational frequencies of C—H bonds of methyl and methylidyne groups and of C—Cl bonds in these compounds, and also by the absence of lowered electron density in C=O bonds in acetic acids — on the contrary, the electron density is increased.*

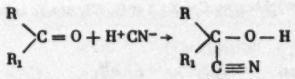
8. Let us turn our attention to some peculiar features of the double bond in C=O, as compared with the double bond in C=C; these confirm the above statements regarding the carbonyl group (see Table 6) [25].

As we pass from No. 4 to No. 1 in a series of compounds containing a C=C bond (Table 6), as indicated in the above discussion, increase of electron density in the bond, mutual approach of nuclei, and increase in bond energy occur. The carbon atoms accumulating in the vicinity, which are equal in electronegativity, do not draw to themselves electrons of the C=C bond: together with these electrons they attract also the nuclei. However, when hydrogen atoms are replaced by atoms that are more electronegative than carbon, namely, chlorine atoms, these already find themselves in a position to draw electrons to themselves: the C=C bond becomes weak and its electrons comparatively labile.

The replacement of one carbon atom of C=C by oxygen, which has high electronegativity (in electronegativity it is exceeded only by fluorine), alters the position greatly. As we have seen, in comparison with the C=C bond the C=O bond is much strengthened and electronized. As we pass along the series of compounds from No. 7 to No. 9 (Table 6), i.e., with replacement of carbon atoms adjacent to C=O by less electronegative hydrogen atoms, the struggle of the carbonyl oxygen for electrons is made easier: together with electrons, the nuclei of C and H atoms are drawn toward it — the whole of the molecule is compacted, electronized. When, however, the hydrogen atoms are replaced by highly electronegative chlorine atoms, in their competition with the very highly electronegative oxygen atom for electrons, these chlorine atoms do not draw electrons away from the oxygen — and neither does the reverse occur: a further compacting of the whole molecule occurs with mutual approach of nuclei, increase in electron density, rise in E and ν, and shortening of r, i.e., increase in the electronization of the C=O bond.**

We must point out that in compounds such as liquid oxoctenol and acetic acid (Table 4) the electronization of the C=O bond is further weakened, as compared with this bond in ketones, owing to the effect of the hydrogen bond $>C=O\cdots H-$; the participation of the carbonyl group of an acid in a hydrogen bond reduces further its reactivity. On the other hand, in systems of the ketene type with their well known extremely high reactivity, the electronization of all the bonds increases sharply, as shown above.

9. The above discussion thows light on the mechanism of reactions of addition to carbonyl compounds, a typical example of which is the reaction mentioned previously:



* Whereas in liquid acetic acid the CO frequencies of the dimer ring and the polymeric chain (in which CO groups occur in the middle and at the end of the chain) lie in the range 1670-1740 cm^{-1} [14], in mono-, di-, and tri-acetic acids they not only do not occur in a lower range, but are in fact found in a somewhat higher range of frequencies [10].

** The described pattern of changes in the double bonds C=C and C=O in Compounds 1-6 and 7-10 (Table 6) emphasizes the characteristic nature of these bonds.

TABLE 5

1. Vibrational Frequencies of Ketene and Other Compounds (cm^{-1})

C=O	C=C	C–H group of CH_2
Ketene 2049 Acetone 1707	Ketene 1895 Ethylene 1621	Ketene 2954, 3015 n-Paraffins 2853, 2908
Increase + 342	Increase + 274	Increase + 99, + 107

2. Vibrational Frequencies of Phosgene, Formaldehyde, and Other Compounds (cm^{-1})

C=O		C–H group of CH_2*	C–Cl group of CCl_2
$Cl_2C=O$ 1808 $(CH_3)_2C=O$ 1707	$H_2C=O$ 1744 $(CH_3)_2C=O$ 1707	$H_2C=O$ 2910c, 2990a CH of n-paraffins 2858s, 2908a	$Cl_2C=O$ 883** Cl_2CH_2 762**
Increase + 101	Increase + 37	Increase + 57 + 82	Increase + 71

3. Vibrational Frequencies of Acetaldehyde, Acetone, and Other Compounds (cm^{-1})

C=O	C–H group of CH_3	
CH_3C-CHO 1720 $(CH_3)_2CO$ 1707	CH_3-CHO 2917c 2966a 3015a CH_3 of n-paraffins 2879s 2938a 2967a	$(CH_3)_2CO$ 2922s 2965a 3006a CH_3 of n-paraffins 2879c 2938a 2967a
Increase + 13	Increase + 38 + 28 + 48	Increase + 43 + 27 + 39

* s – symmetrical vibration; a – antisymmetrical vibration.

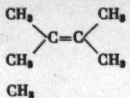
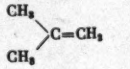
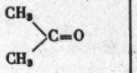
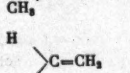
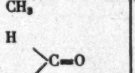
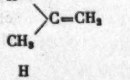
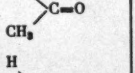
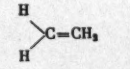
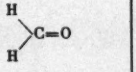
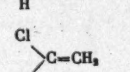
** Only the frequency of the antisymmetrical vibration is given.

The strongly electronized carbonyl bond increases the polarization of H^+/CN^- molecules, causing it to take up the ionic state. The proton, distinguished by high mobility and negligibly small dimensions, initiates reaction by attaching itself to the carbonyl oxygen, which has two unshared electron pairs. The equilibrium of the nucleus-electron system is disturbed and the carbonyl carbon at some moment becomes positive; a CN^- ion naturally attaches itself to it. Reaction, therefore, proceeds in stages in the way indicated.

In the series of compounds in Table 4, the degree of electronization of the bonds increases in the direction from the fatty acids to ketene. It is in this same direction that the reactivity of carbonyl compounds increases in addition reactions, as emphasized by the authors of the hypothesis that we are considering [16, 17]. Hence, this rise in reactivity in this series is associated with rise in the electronization of the C=O bond and adjacent bonds and is not associated in any way with the effects proposed by the authors of this hypothesis (+T in X—C bonds and –I or –T in the C=O bond of the group); not only are these effects not confirmed by direct

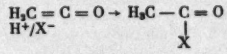
TABLE 6

Frequencies of C = C and C = O Bonds in Various Compounds (cm^{-1})

No.	Compound	C—C	No.	Compound	C—O	Difference of C = O and C = C frequencies
1		1676		—	—	—
2		1658	7		1707	49
3		1648	8		1720	72
4		1621	9		1744	123
5		1611	10		1808	197
6		1571		—	—	—

physical experiments, but on the contrary, experiment reveals the opposite phenomenon.

We will draw attention to one peculiar feature of addition reactions with the extreme member of the series under discussion, ketene: they proceed predominantly at the ethylene bond, not at the carbonyl [26]. This is to be related to the above-indicated higher stability of the carbonyl bond as compared with the ethylene bond and the higher lability of the electrons of the ethylene bond as compared with those of the carbonyl bond. As the C—H bonds are strongly electronized and the electron density of the C = O bond has a certain degree of asymmetry and is somewhat more highly concentrated at the oxygen atom (see above), addition reactions at the ethylene bond of ketene proceed through the same stages and by the operation of similar circumstances as in the above-described case of addition to a carbonyl group:



SUMMARY

By comparison of physical and chemical data on individual characteristic bonds it is shown that the chemical nature of these bonds is dependent on their physical state (the electron-nucleus interactions in them), which is manifested in the experimentally determined parameters of these bonds ν, E, and $\underline{r}$. Taking carbonyl compounds as an example, we have shown that from the strictly correlated changes in these parameters in characteristic bonds it is possible to make an estimate, on an experimental basis, of the electron displacements in the bonds as factors determining the reactivities of these bonds and as factors expressing the structure of the

molecule and the mutual effects of its atoms.

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ATTEMPT TO SET UP A SEMIQUANTITATIVE THEORY OF MUTUAL EFFECTS OF ATOMS IN ORGANIC COMPOUNDS

COMMUNICATION 1. ELECTRONIC CHARGES OF BONDS, ELECTRONEGATIVITIES OF ATOMS, AND THE HEATS OF FORMATION OF SATURATED HYDROCARBONS

G. V. Bykov

According to the classical Butlerov-Markovnikov theory of the mutual effects of atoms, the chemical affinities of the atoms of a molecule depend on the chemical structure of the molecule, the characteristics of the chemical bonds (formed by the union of "units of affinity") depend on the chemical affinities, and the chemical and physical properties of the molecule depend on the characteristics of the bonds. Before modern experimental and theoretical physical methods of investigation were available, study of the links of this chain – chemical structure of the molecule, chemical affinities of atoms, interatomic chemical bonds, chemical and physical properties of the molecule – was confined largely to the first and last. However, although for a long time no satisfactory views existed concerning the true nature of chemical affinity and the chemical bond, chemists, by comparing the properties of molecules with their structural characteristics, were able to draw many valuable conclusions about chemical affinity and chemical bonds, and these conclusions were subsequently confirmed by physical methods of investigation.

In spite of the enormous success of theoretical chemistry based on these methods, there is at present no theory of mutual effects of atoms which would enable us to treat the mass of varied factual material in organic chemistry from a unified point of view. In the author's opinion, the creation of such a theory is hindered by an adherence to out-of-date doctrines with the associated lack of new ideas that might be used as a basis for the theory, and also by the existence of the view, tacitly accepted by most chemists and sometimes openly expressed, that the main theoretical problems of organic chemistry can be solved only by the methods of quantum mechanics. In speaking of out-of-date doctrines, above all the author has in mind the assertion – the position of which is already badly shaken in the case of π-bonds, but is still stubbornly maintained in the case of σ-bonds – that the chemical bond is formed by an electron cloud consisting of a whole number of electrons. As regards quantum methods in organic chemistry, the author is far from any underestimation of their value, but he considers that there are no grounds for a nihilistic attitude to the historically justified methods of the classical theory of chemical structure, that even now these methods can make a valuable contribution to the development of the theory of organic chemistry, and that theoretical chemistry can only lose if one set of methods is placed in opposition to the other, but will gain much if the methods are regarded as complementary and used as such.

In his attempt to set up a theory of mutual effects of atoms, the author has turned his attention to some new theoretical concepts (see below) and to some old methods – to the examination of chemical affinity and chemical bonds on the basis of the correlation of properties with the chemical structure of the molecule and to the advancing of hypotheses, the drawing of inferences from these hypotheses, and the comparison of these inferences with the facts. The object of the present investigation was to prove the correctness and fruitfulness of this new approach and the possibility of using methods of the classical theory of chemical structure in the solution of theoretical problems of organic chemistry. In this paper, therefore, only the basic ideas of the author's theory will be expounded and illustrated, and the more detailed development of these ideas will be made in a future paper. The reader will find further material on this question, including some remarks on its history, in another article by the author [1].

Concept of the Electronic Charge of a Bond, and the Basic Assumptions. By the electronic charge of a bond we mean the share of the total σ- or π-electron cloud of the molecule that is to be assigned to the given bond. In general, the electronic charge of a bond is not equal to a whole number of electrons (Fig. 1). As the chemical affinity of atoms in their valence states is now regarded as the energy of attraction of valence electrons by atom cores [2], it is clear that the electronic charge of a bond must be determined to some extent — or even predominantly — by the electronegativities of the atoms in their valence states. The characteristics of a bond (length, energy, force constant, etc.) naturally depend in one way or another on its electronic charge, but it may be assumed that the properties of a bond are determined mainly by its electronic charge and, to a first approximation, all other influences may be neglected in the consideration of this relationship.

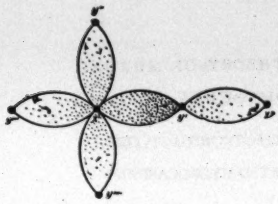


Fig. 1. Diagrammatic representation of the distribution of electronic charges in the bonds of a molecule of the methanol type. Closer packing of the points corresponds to higher electronic charge. This representation serves also to show the polarity of the bonds.

As we shall see, both of these assumptions are justified in that they make it possible to carry out quantitative calculations. In these calculations we shall use, in the first place, some very simple semi-empirical equations, which express the relation of the electronic charge of a bond to the electronegativities of the atoms or to some of the properties of the bond. The investigation of very simple equations must be regarded as expedient from the chemist's point of view because a clear physical meaning is then retained to the greatest possible extent in the formulas, and elementary methods are developed for calculating the electronic structure and properties of the molecule; there is still always the possibility of developing a more precise and more complex form of functional relationship.

The chemical properties of organic compounds — the tendency to react and the directions in which they react — depend largely on the general distribution of valence-electron charges among the bonds of the molecule and on the electronic charges of individual bonds. Study of chemical properties from this point of view must, therefore, be preceded by the development of methods of calculating or, at least, estimating the electronic charges of the bonds from the electronegativities of the atoms and the physical characteristics of the bonds.

Relation between Electronegativities of Atoms and Electron Charges of Bonds. Let us suppose that the atoms X' and Y' (Fig. 1) contribute $n_{X'}$ and $n_{Y'}$ electrons respectively to the general valence-electron cloud of the molecule. Let us assume that the electron cloud attributable to the valence electrons of any given atom is distributed among all its bonds with other atoms in amounts directly proportional to the electronegativities of these atoms, then the share $A_{X'}$ of the electronic charge of the bond X'—Y' contributed by atom X' will be proportional to the number of its valence electrons $n_{X'}$ and the electronegativity $E_{Y'}$ of the atom Y' and will be inversely proportional to the sum of the electronegativities ΣE_Y of the atoms directly united to X'.

$$A_{X'} = \frac{n_{X'} E_{Y'}}{\Sigma E_Y} . \qquad (1)$$

An analogous formula can be written for $A_{Y'}$ — the share of the electronic charge of the bond X'—Y' contributed by the atom Y'. The total electronic charge $A_{X'Y'}$ will be expressed by the formula

$$A_{X'Y'} = A_{X'} + A_{Y'} = \frac{n_{X'} E_{Y'}}{\Sigma E_Y} + \frac{n_{Y'} E_{X'}}{\Sigma E_X} . \qquad (2)$$

If X' is a univalent atom, then it is clear from Equation 1 that in the σ-electron charge of the bond X'–Y' its share is equal to one σ-electron, but in the π-electron charge its share is zero.

It will be seen from Equation 2 that absolute electronegativities are not required for the calculations, relative values being adequate. The hydrogen scale, on which the electronegativities of the various elements are referred to that of hydrogen (unity), is particularly convenient. It will be obvious that relative electronegativity is a dimensionless quantity. Table 1 gives three electronegativity scales: Huggins' (a corrected version of Pauling's well known scale) [3], Gordy's [4], and Nekrasov's [2], which are derived from different premises.

TABLE 1

Relative Electronegativities of Various Elements ($E_H = 1.00$)

Author of scale	C	N	O	F	Cl	Br	I
Huggins*	1.18	1.39	1.59	1.77	1.43	1.34	1.20
Gordy*	1.20	1.40	1.62	1.85	1.39	1.29	1.15
Nekrasov	1.19	1.71	2.03	2.31	1.43	1.37	1.24

* The data of Huggins and Gordy were recalculated to the hydrogen scale by the author.

Nekrasov's value of the electronegativity of carbon E_C is to be preferred, since it is the arithmetic mean of the values on the other two scales, but Nekrasov's values for nitrogen, oxygen, and fluorine are considerably higher than the values given by the scales of Huggins and Gordy. Hence, when making use of Nekrasov's scale in our further calculations, we shall pay attention to the possibility of checking it and improving its accuracy.

The composition and chemical structure of a molecule affects the electronegativities of its atoms. It is possible to make an estimate of the electronegativities of carbon atoms in molecules of saturated hydrocarbons (see later). We may formulate the following rule: of the atoms of a given element, the highest electronegativity is possessed by the one that is directly united to the more highly electronegative atoms. The highest electronegativity is possessed by quaternary carbon atoms, and the lowest – by primary carbon atoms. For the simplified calculation of the electronegativities of carbon atoms in saturated hydrocarbons, the following empirical formula may be used:

$$E_C = 1.190 + \frac{\sum_{i}^{N_0} N_i^2}{3^{6-N_0} \cdot 10^2}, \qquad (3)$$

in which N_0 is the number of carbon atoms directly united with the given C atom, these directly united carbon atoms being distinguished by the numbers 1, 2, etc., =(in general) $\underline{i}$; $N_{\underline{i}}$ is the number of carbon atoms directly united to the carbon atom numbered $\underline{i}$. In the further treatment we shall employ a nomenclature which we shall illustrate by an example. We shall write the tertiary carbon of 2,2,3-trimethylbutane as C_3^{114}: the lower index is N_0, and the upper index indicates that two of the carbon atoms to which the tertiary carbon is attached are primary ($N_1 = N_2 = 1$) and one is quaternary ($N_3 = 4$). We have

$$E_{C_3^{114}} = 1.190 + \frac{1^2 + 1^2 + 4^2}{3^{3-3} \cdot 10^2} = 1.210.$$

The electronegativities given in Table 2 were calculated from Equation 3.

TABLE 2

Relative Electronegativities of Carbon Atoms in Saturated Hydrocarbons

C_1	E_C	C_2	E_C	C_3	E_C	C_4	E_C
C_1^1	1.190	C_2^{11}	1.191	C_3^{111}	1.193	C_4^{1111}	1.203
C_1^2	1.190	C_2^{12}	1.192	C_3^{112}	1.197	C_4^{1112}	1.213
C_1^3	1.191	C_2^{13}	1.194	C_3^{113}	1.202	C_4^{1113}	1.230
C_1^4	1.192	C_2^{14}	1.196	C_3^{114}	1.210	C_4^{1114}	1.253

In Table 3 a comparison is made between A'— σ-electron charges of C—C bonds of saturated hydrocarbons calculated from Equation 2 on the assumption that $E_C = 1.19$ for all carbon atoms— and A"— the charges calculated from the same equation on the assumption that the electronegativities of carbon are as in Table 2.

New Additive Scheme for the Calculation of Heats of Formation of Saturated Hydrocarbons. Let us assume that the energy of a σ-bond is directly proportional to its σ-electron charge:

$$D_{XY} = \Delta^h_{XY} A_{XY}, \qquad (4)$$

in which D_{XY} is the energy and A_{XY} is the σ-electron charge of the given X—Y bond; Δ^h_{XY} is the proportionality coefficient and is the fraction of the bond energy attributable to one σ-electron— for this reason we shall call it the specific electronic energy of the bond. For a saturated hydrocarbon C_nH_{2n+2} the following equation will hold:

$$\Delta^h_{CC}\sum A_{CC} + \Delta^h_{CH}\sum A_{CH} = \sum D_{CC} + \sum D_{CH}$$

or

$$\Delta^h_{CC}\sum A_{CC} + \Delta^h_{CH}\sum A_{CH} = (\Delta H^\circ_{298.16}\,(at))_{C_nH_{2n+2}}, \qquad (5)$$

in which $(\Delta H^\circ_{298.16}\,(at))_{C_nH_{2n+2}}$ * is the heat of atomization of the given gaseous hydrocarbon, which is equal in absolute magnitude but opposite in sign to the heat of formation of the hydrocarbon from its atoms. As is well known,

* In the further treatment we shall write $H^{at}_{C_nH_{2n+2}}$ in place of this awkward expression.

$$H^{at}_{C_nH_{2n+2}} = H^{el}_{C_nH_{2n+2}} + (2n+2)\,L_H + nL_C, \qquad (6)$$

in which $H^{el}_{C_nH_{2n+2}}$ is the heat of decomposition of the hydrocarbon into its elements, which is equal in magnitude but opposite in sign to its heat of formation from its elements, L_H is the heat of atomization of hydrogen, and L_C is the heat of atomization of carbon. In the course of atomization each carbon atom must take four σ-electrons, and therefore

$$L_C = 4\Delta^{h}_{CC}. \qquad (7)$$

TABLE 3

σ-Electron Charges of C–C bonds in Saturated Hydrocarbons (in electrons)

Bond	A'	A''	Bond	A'	A''
C_1^1–C_1^1	2.272	2.272	C_3^{113}–C_3^{113}	2.083	2.098
C_1^2–C_2^{11}	2.223	2.223	C_3^{114}–C_4^{1113}	2.042	2.078
C_1^3–C_3^{111}	2.178	2.180	C_4^{1114}–C_4^{1114}	2.000	2.076
C_1^4–C_4^{1111}	2.136	2.145	C_1^1–H	1.955	1.955
C_2^{12}–C_2^{12}	2.173(5)	2.174(4)	C_1^4–H	1.955	1.952*
C_2^{13}–C_3^{112}	2.128	2.135	C_2^{14}–H	1.913	1.908**
C_2^{14}–C_4^{1112}	2.088	2.104	C_3^{114}–H	1.875	1.867***

*In 2,2-dimethylpropane.
**In 2,2-dimethylbutane.
***In 2,2,3-trimethylbutane.

Taking Equations 6 and 7 into account we may rewrite Equation 5 as follows:

$$\Delta^{h}_{CC}\sum A_{CC} + \Delta^{h}_{CH}\sum A_{CH} = H^{el}_{C_nH_{2n+2}} + (2n+2)\,L_H + 4n\Delta^{h}_{CC}. \qquad (8)$$

For methane, taking account of the fact that there are no C–C bonds and ΣA_{CH} is equal to 8 σ-electrons, we may write the equation as

$$\Delta^{h}_{CH}\cdot 8 = H^{el}_{CH_4} + 4L_H + 4\Delta^{h}_{CC}.$$

After insertion of values of $H^{el}_{CH_4}$ (17.889 kcal/mole) and L_H (52.089 kcal/g-atom)* from tables, we obtain:

*Here and later we take values of $H^{el}_{C_nH_{2n+2}}$ and L_H from the tables of Rossini and coworkers [5] without recalculation of heats of formation from graphite into heats of formation from diamond.

$$\Delta^{h}_{CH} = 28.28 + 0.5\Delta^{h}_{CC}. \tag{9}$$

For the total σ-electron charges of C—C and C—H bonds in hydrocarbons, the following equation is valid:

$$\sum A_{CH} = N_{\sigma} - \sum A_{CC}, \tag{10}$$

in which N_{σ} is the number of σ-electrons in the molecule. In the saturated hydrocarbon C_nH_{2n+2}

$$N_{\sigma} = 4n + (2n + 2) = 6n + 2. \tag{11}$$

Let us substitute in Equation 8 the values of Δ^{h}_{CH} from Equation 9 and ΣA_{CH} from Equation 10 and rearrange the resulting equation, leaving only terms containing ΣA_{CC} on the left-hand side:

$$\sum A_{CC}(0.5 \quad \Delta^{h}_{CC} - 28.28) = H^{el}_{C_nH_{2n+2}} + (2n + 2)\, L_H - 28.28\, N_{\sigma} + \\ + (4n - 0.5N_{\sigma})\, \Delta^{h}_{CC} \tag{12}$$

For ethane $H^{el}_{C_2H_6} = 20.236$, n = 2, and $N_{\sigma} = 14$; substituting these values and also the numerical value of L_H in Equation 12, we obtain

$$A_{C_1C_1}\,(0.5\,\Delta^{h}_{CC} - 28.28) = \Delta^{h}_{CC} - 63.15. \tag{13}$$

Combining Equations 12 and 13, we may eliminate Δ^{h}_{CC}. For this purpose we shall denote the σ-electron charge of the C—C bond of ethane as

$$A_{C_1C_1} = 2 + z. \tag{14}$$

Substituting the value of $A_{C_1C_1}$ from Equation 14 into Equation 13, we obtain:

$$z\,(0.5\,\Delta^{h}_{CC} - 28.28) = -6.59. \tag{15}$$

The averaged σ-electron charge of C—C bonds in saturated hydrocarbons is

$$\overline{A}_{CC} = \frac{\Sigma A_{CC}}{n-1}, \tag{16}$$

but on analogy to Equation 14

$$\overline{A}_{CC} = 2 + \alpha z. \tag{17}$$

From Equations 17, 14 and 16 we find that

$$\alpha = \frac{\overline{A}_{CC} - 2}{A_{C_1C_1} - 2} = \frac{\frac{\Sigma A_{CC}}{n-1} - 2}{A_{C_1C_1} - 2}. \qquad (18)$$

In the further treatment we shall refer to α as the ethane coefficient of the hydrocarbon C_nH_{2n+2}.

From Equations 16 and 17 it follows that

$$\sum A_{CC} = \overline{A}_{CC} \cdot (n-1) = (2 + \alpha z)(n-1). \qquad (19)$$

Substituting this value of ΣA_{CC} in Equation 12 and rearranging, we obtain:

$$\begin{aligned}(n-1)\,\Delta^h_{CC} - 28.28\,(2n-2) + \alpha z\,(n-1)\,(0.5\,\Delta^h_{CC} - 28.28) = \\ = H^{el}_{C_nH_{2n+2}} + (2n+2)\,L_H - 28.28\,N_\sigma + (4n - 0.5\,N_\sigma)\,\Delta^h_{CC}.\end{aligned} \qquad (20)$$

Substituting the value N_σ from Equation 11 and the numerical value of L_H in Equation 20, we obtain:

$$\alpha z\,(n-1)\,(0.5\,\Delta^h_{CC} - 28.28) = H^{el}_{C_nH_{2n+2}} - 8.94\,(n+1). \qquad (21)$$

Division of Equation 21 by Equation 15 gives:

$$\alpha = \frac{8.94\,(n+1) - H^{el}_{C_nH_{2n+2}}}{6.59\,(n-1)}. \qquad (22)$$

Since ethane coefficients can be calculated from Equation 18, using electronegativity data for the calculation of A_{CC}, we have obtained an equation that relates the heats of formation of gaseous saturated hydrocarbons from their elements to the electronegativities of the carbon atoms. Calculations based on this equation will enable us to judge whether the assumptions made in its derivation are correct or not.

As will be seen from Table 4 (Nos. 1-21), there is a definite correlation between the values of ethane coefficients calculated from heats of formation and those calculated from electronegativities. The greatest discrepancy is found for hydrocarbons containing quaternary and tertiary carbon atoms (Nos. 7, 20, 21). Taking the value of the σ-electron charge of the C–C bond in ethane given in Table 3 ($A_{C_1C_1}$ = 2.272 electrons) and using the ethane coefficients calculated from heats of formation, we may calculate the total σ-electron charges in the various hydrocarbons from Equation 19. The agreement of the values of ΣA_{CC}(H) obtained by this mixed method of calculation with ΣA_{CC}(E) is quite satisfactory. The greatest discrepancies are found for Nos. 20 and 21, which contain quaternary carbon atoms.

From ΣA_{CC}(H) we can obtain – in some cases (Nos. 2, 4, 7) directly, and in others by simple calculations – values of the σ-electron charges of individual bonds. By substitution of these values in Equation 2, we may estimate the electronegativities of carbon atoms occupying structurally different places in the molecule. The results obtained in this way are generalized in Equation 3. In the three lowest lines in Table 4 (Nos. 7a, 20a, and 21a) we give total σ-electronic charges ΣA_{CC}(E), for the calculation of which we used electronegativities

TABLE 4

Ethane Coefficients, Total σ-Electron Charges of C–C Bonds, and Heats of Formation of Saturated Hydrocarbons [a]

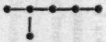
No.	Formula	n	a_H	a_E	Δ_a	$\Sigma A_{CC}(H)$	$\Sigma A_{CC}(E)$	Δ_A	$H^{gl}_{C_nH_{2n+2}}$ (exp)	$H^{gl}_{C_nH_{2n+2}}$ (calc)	Δ_H
1		2	1	1	0.000	(2.272)	2.272	0.00	20.236	(20.23)	0.00
2		3	0.831	0.819	−0.012	4.52	4.45	−0.07	24.82	24.97	+0.15
3		4	0.736	0.759	+0.023	6.60	6.62	+0.02	30.15	29.69	−0.46
4		4	0.635	0.653	+0.018	6.52	6.53	+0.01	32.15	31.79	−0.36
5		5	0.708	0.729	+0.021	8.77	8.79	+0.02	35.00	34.42	−0.58
6		5	0.634	0.649	+0.015	8.69	8.71	+0.02	36.92	36.53	−0.39
7		5	0.530	0.500	−0.030	8.58	8.54	−0.04	39.67	40.46	+0.79
8		6	0.687	0.710	+0.023	10.93	10.97	+0.04	39.96	39.19	−0.77
9		6	0.636	0.647	+0.011	10.86	10.88	+0.02	41.66	41.26	−0.40
10		6	0.655		−0.008	10.89		−0.01	41.02		+0.24

TABLE 4 (Continued)

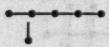
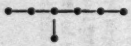
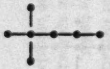
No.	Formula	n	ε_H	ε_E	Δ_ε	$\Sigma A_{CC}(H)$	$\Sigma A_{CC}(E)$	Δ_A	$H^{el}_{C_nH_{2n+2}}$ (exp)	$H^{el}_{C_nH_{2n+2}}$ (calc)	Δ_H
11		6	0.610	0.583	−0.027	10.83	10.79	−0.04	42.49	43.37	+0.88
12		6	0.554	0.528	−0.026	10.75	10.72	−0.03	44.35	45.18	+0.83
13		7	0.674	0.699	+0.025	13.10	13.14	+0.04	44.89	43.88	−1.01
14		7	0.631		+0.015	13.03		+0.02	46.60		−0.62
15		7	0.647	0.646	−0.001	13.06	13.05	−0.01	45.96	45.98	−0.02
16		7	0.662		−0.016	13.08		−0.03	45.34		+0.64
17		7	0.605		−0.008	12.99		−0.02	47.62		+0.45
18		7	0.588	0.593	+0.005	12.96	12.97	+0.01	48.30	48.07	−0.23
19		7	0.562	0.546	−0.016	12.92	12.89	−0.03	49.29	49.93	+0.64

TABLE 4 (Continued)

No.	Formula	n	α_H	α_E	Δ_α	$\Sigma A_{CC}(H)$	$\Sigma A_{CC}(E)$	Δ_A	$H^{el}_{C_nH_{2n+2}}$ (exp)	$H^{el}_{C_nH_{2n+2}}$ (calc)	Δ_H
20		7	0.591	0.546	—0.045	12.96	12.89	—0.07	48.17	49.93	+1.76
21			0.571	0.493	—0.078	12.93	12.80	—0.13	48.96	52.03	+3.07
7a		5	0.530	0.533	+0.003	8.58	8.58	0.00	39.67	39.60	—0.07
20a		7	0.591	0.594	+0.003	12.96	12.97	+0.01	48.17	48.03	—0.14
21a			0.571	0.566	—0.005	12.93	12.92	—0.01	48.96	49.14	+0.18

* n — number of carbon atoms; α_H — ethane coefficient calculated from heats of formation $H^{el}_{C_nH_{2n+2}}$ (expt); α_E — ethane coefficient calculated from data in Column 2, Table 3; $\Delta_\alpha = \alpha_E - \alpha_H$; $\Sigma A_{CC}(H)$ — total σ-electron charge of hydrocarbon calculated by substitution of α_H and z = 0.272 in Equation 19; ΣA_{CC} — total σ-electron charge of hydrocarbon calculated from data in Column 2, Table 3; $\Delta_A = \Sigma A_{CC}(E) - \Sigma A_{CC}(H)$; $H^{el}_{C_nH_{2n+2}}$ (expt) — experimental heat of formation of gaseous saturated hydrocarbon from elements [5]; $H^{el}_{C_nH_{2n+2}}$ (calc) — heat of formation calculated from Equation 22 with the use of values of α_E; $\Delta = H^{el}_{C_nH_{2n+2}}(\text{calc}) - H^{el}_{C_nH_{2n+2}}(\text{expt})$.

calculated from Equation 3. In these lines the values of ΣA_{CC} and α calculated by different methods agree very much better than in the lines Nos. 7, 20, and 21.

Of particular importance is the comparison of heats of formation $H^{el}_{C_nH_{2n+2}}$ determined experimentally with those calculated by Equation 22 with α_E substituted for α. The discrepancies between calculated and experimental values, although outside experimental error, are of the same order as the discrepancies between the values calculated by the empirical additive scheme of Tatevsky [6] and the experimental values. It must be remembered that the ratio of absolute errors

$$\frac{dH^{el}_{C_nH_{2n+2}}}{d\alpha} = -6.59(n-1)$$

is very high, so that results obtained by the use of a crude scheme for the calculation of α_E must be regarded as quite satisfactory. With improvement in the scheme of calculating α_E (three lowest lines of the table), close agreement between the calculated and experimental values of $H^{el}_{C_nH_{2n+2}}$ is obtained. Hence, the results confirm the rationality of the scheme of calculation used and, what is most important, of the theoretical postulates on which the scheme is based.

Using the values of $\Sigma A_{CC}(H)$ and $H^{el}_{C_nH_{2n+2}}$ (expt) from the relevant columns of Table 4 (Nos. 1-21), we may calculate Δ^h_{CC} from Equation 12 and then Δ^h_{CH} with aid of Equation 9. The results obtained were

$$\Delta^h_{CC} = 8.054 \pm 0.007 \text{ *and} \Delta^h_{CH} = 32.308 \pm 0.003 \text{ kcal/q} \cdot \text{electron}$$

$H^{el}_{C_nH_{2n+2}}$ may then be calculated from Equation 8. We do not give the results of this calculation because they do not differ significiantly (the mean discrepancy is 0.023 kcal/mole) from the values obtained from Equation 22. These results show that it is possible to construct an additive scheme, which is new in principle, for the calculation of heats of formation and linearly related quantities, the terms added being products of electronic charges of bonds and specific electronic energies.

SUMMARY

1. The author proposes to construct an electronic theory of the mutual effects of atoms in organic compounds on the basis of the concept of the electronic charge of a bond, which in the general case is not equal to a whole number of electrons.

2. An equation is proposed which expresses the dependence of electronic charges of bonds on the electronegativities of the atoms. An equation is derived for the calculation of heats of formation of gaseous saturated hydrocarbons from their elements with the aid of values of electronic charges of bonds calculated by the first equation. The agreement found between the experimental values of heats of formation and values calculated with these equations confirms the theoretical postulates on which they were based. In particular, confirmation is found for the postulate that the energies of the σ-bonds are, to the first approximation, directly proportional to their σ-electron charges. A new additive scheme is proposed for the calculation of heats of

*According to Equation 7 we obtain $L_C = 4\Delta^h_{CC} = 32.216$ kcal/g-atom for the heat of atomization of carbon, although this heat of atomization is most usually given values ranging from 124 to 170 kcal/g-atom. Our value must, of course, appear paradoxical. Although it would be possible to advance several more arguments in its favor, we consider it desirable to give separate consideration to the whole question of the heat of atomization of carbon which is of secondary importance for the present investigation. The author proposes to do this in the near future.

formation of saturated hydrocarbons. In this scheme the terms of the summation are products of σ-electron charges of bonds and specific electronic energies.

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REACTIONS OF FLUORO OLEFINS

COMMUNICATION 6. REACTIONS OF PERFLUOROISOBUTENE AND PERFLUOROPROPENE WITH NUCLEOPHILIC REAGENTS

I. L. Knunyants, L. S. German and B. L. Dyatkin

In the study of reactions of fluoro olefins with nucleophilic reagents (alcohols, thiols, amines) the examples taken have been mainly fluoro derivatives of ethylene. Of the higher fluoro olefins, perfluoropropene has been investigated in its reactions with alcohols, thiols, and amines [1], in which it undergoes addition in accordance with the electronic interpretation of Markovnikov's rule:

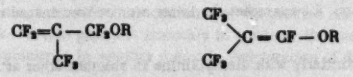
$$CF_3\overset{\delta-}{C}F=\overset{\delta+}{C}F_2 + H^+X^- \longrightarrow CF_3CFHCF_2X$$

X=OAlk, SAlk, $(C_2H_5)_2N$, C_6H_5O

In the reactions with alcohols, products were isolated (in the form of dibromides) which were formed by substitution of one fluorine of the perfluoropropene molecule by an alkoxy group. It was shown that the formation of unsaturated compounds was not the result of a secondary reaction (elimination of hydrogen fluoride from the corresponding addition products).

The reactions of C_4 fluoro olefins with nucleophilic reagents have scarcely been investigated. Only the reaction of perfluoroisobutene with ethanol has been studied; this proceeds at room temperature in absence of alkaline catalysts, but only the addition product – the structure of which was not proved – was isolated [2].

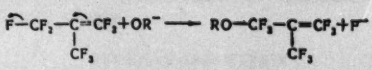
In a detailed study of the reaction of perfluoroisobutene with alcohols, we found that, in addition to the main reaction products (alkyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ethers), unsaturated compounds were formed which corresponded in composition to products formed by the replacement of one fluorine of the perfluoroisobutene molecule by an alkoxy group. For these compounds, two structures may be proposed:



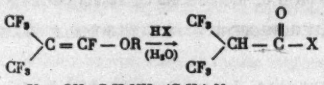
(I) or (II)

R = CH_3, C_2H_5.

At first sight the structure (I) appears to be the more probably because it may be supposed that π,σ-conjugation occurs in the perfluorobutene molecule and can result in allyl rearrangement:



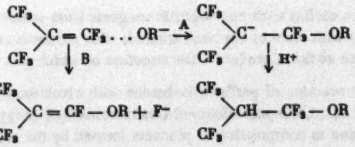
However, the reactions of the alkoxyisobutenes obtained correspond to the structure (II); thus, hydrolysis with concentrated sulfuric acid in presence of silica converts them into 3,3,3-trifuloro-2-(trifluoromethyl) propionic esters, and by the action of amines they are converted into the corresponding amides:



X = OH, C_5H_5NH, $(C_2H_5)_2N$.

The resulting alkoxyisobutenes therefore, have the structure of alkyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ethers; their formation can be represented either as direct replacement of a fluorine atom by alkoxyl or as the result of elimination of hydrogen fluoride from alkyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ethers which are formed in the first place.

It is actually found that, when treated with a suspension of KOH in ether, alkyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ethers lose HF with formation of alkyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ethers. However, the formation of the latter by reaction of perfluoroisobutene with alcohols must be regarded as the result of direct replacement of an F atom in a CF_2 group, for under the conditions of reaction (absence of alkali) alkyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ethers are stable. Hence, we have here an unusual case of the replacement of a vinylic chloride atom, which, according to generally accepted ideas, should be inert. This phenomenon may be explained by electronic depletion and the high polarization of the π-bond in perfluoroisobutene due to the presence of two CF_3 groups on one of the carbon atoms. For this reason the polarizability of the π-bond is low and stabilization of the reaction complex originally formed proceeds not only by addition of a proton (Path A), but also by elimination of a fluoride ion (Pathe B):

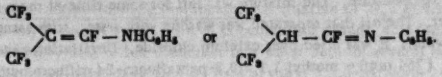


The character of the double bond of perfluoroisobutene is largely preserved in alkyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ethers; for example, the latter are not brominated even when heated with bromine at 100° for a long time.

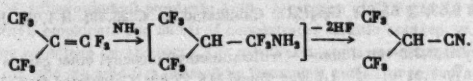
Perfluoroisobutene reacts similarly with diethylamine in absolute ether at room temperature, and here the sole reaction product is N,N-diethyl-1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenylamine $(CF_3)_2C{=}CF{-}N{=}(C_2H_5)_2$; its formation may be explained by elimination of hydrogen fluoride from the originally formed α,α-difluoro-amine $(CF_3)_2CH{-}CF_2{-}N(C_2H_5)_2$ or by direct replacement of the vinylic fluorine atom by the diethylamino group. Attempts that we made to direct the reaction toward the formation of the α,α-difluoro amine (addition of diethylamine at low temperature to perfluoroisobutene) were unsuccessful.

N,N-diethyl-1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenylamine does not react with bromine, does not form salts with acids, and is extremely readily hydrolyzed with formation of N,N-diethyl-3,3,3-trifluoro-2-

(trifluoromethyl) propionamide. Reaction of perfluoroisobutene with aniline gives 3,3,3-trifluoro-2-(trifluoromethyl) propionanilide, and an intermediate product can be isolated which, according to the analytical data may be assigned one of the two structures:

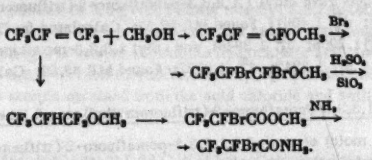


Reaction of perfluoroisobutene with ammonia in ethereal solution gives 3,3,3-trifluoro-2-(trifluoromethyl) propionitrile:



The corresponding amide was obtained as by-product.

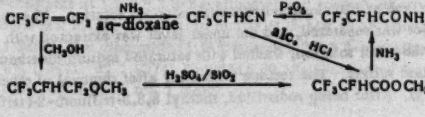
As regards the reactions of perfluoropropene with alcohols and amines, which have already been partially investigated, we have now succeeded in showing that, in the reaction of perfluoropropene with alcohols, the vinylic fluorine atom is again replaced. This was proved as follows:



The obtaining of derivatives of 2-bromo-2,3,3,3-tetrafluoropropionic acid provides unequivocal proof of the structure of the alkoxyfluoropropenes obtained.

As was shown previously, in the reaction of perfluoropropene with diethylamine in an aqueous medium under pressure, N,N-diethyl-1,3,3,3-tetrafluoropropionamide is formed [1]. By carrying out this reaction in an absolute medium under atmospheric pressure, we succeeded in isolating the intermediate products $CF_3CF=CFN(C_2H_5)_2$ and $CF_3CFHCF_2N(C_2H_5)_2$, though the closeness in boiling point did not permit us to separate them. We succeeded in showing indirectly that the proportion of the propenylamine in the mixture was about 70%.

There is a reference in the literature to the formation of 2,3,3,3-tetrafluoropropionitrile by reaction between perfluoropropene and ammonia, but neither the constants of the product nor the reaction conditions are described [3]. We showed that this reaction proceeds smoothly in aqueous-dioxane solution. For comparison we prepared 2,3,3,3-tetrafluoropropionitrile by another method: dehydration of the corresponding amide:



EXPERIMENTAL

Reaction of Perfluoroisobutene with Alcohols

Reaction with Methanol. Gaseous perfluoroisobutene (67 g, i. e., 0.35 mole) was passed into stirred methanol (50 ml) at room temperature. The mixture was left for some time at room temperature, and was then poured into cold water. The oil that separated was washed with water, with saturated sodium bicarbonate solutions, and again with water; it was dried over calcium chloride. Distillation gave the following fractions: Fraction I, b.p. 68.5-70.5° (754 mm) – methyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether, yield 50.7 g (64.7%); Fraction II, b.p. 101-104° (754 mm) – methyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether, yield 5.7 g (8%). This substance decolorized a solution of potassium permanganate in acetone.

After redistillation, methyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether had the following constants: b.p. 69.5-70° (754 mm); n_D^{20} 1.283; d_4^{20} 1.5000; Found MR 27.41; Calculated* for $C_5F_8H_4O$ MR 28.05

Found %: C 25.83; H 1.63; F 65.65; $C_5F_8H_4O$. Calculated %: C 25.88; H 1.73; F 65.49.

Redistillation of methyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether gave a substance having b.p. 101-102° (754 mm); n_D^{20} 1.3170; d_4^{20} 1.5078; Found MR 27.65; Calculated for $C_5F_7H_3O$ MR 27.45

Found %: C 28.38; H 1.61; F 62.72; $C_5F_7H_3O$. Calculated %: C 28.32; H 1.43; F 62.71.

Reaction with Ethanol. The procedure was as for methanol. Reaction between 40.6 g (0.27 mole) of perfluoroisobutene and 100 ml of ethanol gave 26.4 g (53%) of ethyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether, b.p. 84-86° (749 mm) and 5.0 g (10.8%) of ethyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propenyl ether, b.p. 110-114° (749 mm).

Redistillation of these products gave ethyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether, b.p. 83.5-84° (763 mm); n_D^{20} 1.2950; d_4^{20} 1.4061; Found MR 32.67; Calculated for $C_6F_8H_6O$ MR 32.67 (the literature [2] gives b.p. 83° (743 mm); n_D^{20} 1.2908; d_4^{20} 1.3946), and ethyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether b.p. 113.5-114° (763 mm); n_D^{20} 1.3242; d_4^{20} 1.3932; Found MR 32.52; Calculated for $C_6F_7H_5O$ MR 32.06.

Dehydrofluorination of Alkyl 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl) propyl Ethers

1. A mixture of 8 g (0.034 mole) of methyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether, 6 g (0.10 mole) of potassium hydroxide powder, and 50 ml of ether was boiled with stirring for three hours. The solution was filtered, ether was distilled off, and distillation of the residue gave 4.4 g (60%) of methyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether, b.p. 101-103° (744 mm) and n_D^{20} 1.3182.

2. The reaction was carried out as in the preceding experiment. Reaction between 16 g (0.065 mole) of ethyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether and 6.4 g (0.11 mole) of potassium hydroxide in 50 ml of absolute ether gave 11.6 g (79.1%) of ethyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether, b.p. 113-115° (756 mm). After redistillation its constants were: b.p. 114-115° (745 mm) n_D^{20} 1.3262; d_4^{20} 1.3994; Found MR 32.62; Calculated for $C_6F_7H_5O$ MR 32.06.

Found %: C 31.92; H 2.34; F 59.04 $C_6F_7H_5O$. Calculated %: C 31.87; H 2.23; F 58.82

Hydrolysis of Alkyl 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl) propyl Ethers

Methyl 3,3,3-Trifluoro-2-(trifluoromethyl) propionate. A mixture of 42 g (0.18 mole) of methyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl) propyl ether, 13 ml of concentrated sulfuric acid (sp. gr. 1.82), and 9 g of glass powder was heated in an autoclave at 120° for ten hours with constant rotation. The reaction mixture was then poured onto ice, the lower layer was separated, and the upper layer was extracted with ether. The layer first separated was combined with the ether solution, washed with saturated sodium bicarbonate solution and then with water, and dried over magnesium sulfate. The residue remaining after removal of ether came over at 88-89.5° (743 mm); yield 29.4 g (77.5%). After being redistilled, methyl 3,3,3-trifluoro-2-(trifluoromethyl) propionate

* In all cases the atomic refraction of fluorine was taken as 1.24.

had b.p. 89° (743 mm); n_D^{20} 1.3070; d_4^{20} 1.4470; Found MR 27.72; Calculated for $C_5F_6H_4O_2$ MR 27.78.

Found %: C 28.57; H 1.91 $C_5F_6H_4O_2$. Calculated %: C 28.48; H 1.91

Ethyl 3,3,3-Trifluoro-2-(trifluoromethyl) propionate. A mixture of 24.6 g (0.10 mole) of ethyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl)-propyl ether, 8 ml of concentrated sulfuric acid (sp. gr. 1.82), and 5 g of glass powder was heated in flask fitted with reflux condenser in a water bath for several hours. Treatment of the product as in the preceding experiment gave 15.7 g (70%) of ethyl 3,3,3-trifluoro-2-(trifluoromethyl) propionate, b.p. 101-103° (755 mm). After redistillation the constants were: b.p. 102.5° (750 mm); n_D^{20} 1.3161; d_4^{20} 1.3554; Found MR 32.45; Calculated for $C_6F_6H_6O_2$ MR 32.40.

Found %: C 32.05; H 2.79; F 50.63 $C_6F_6H_6O_2$. Calculated %: C 32.15; H 2.70; F 50.87.

3,3,3-Trifluoro-2-(trifluoromethyl) propionic Acid. A mixture of 33.6 g (0.15 mole) of ethyl 3,3,3-trifluoro-2-(trifluoromethyl) propionate and 56 ml of concentrated sulfuric acid (sp. gr. 1.82) was heated at 100° in a constantly rotating autoclave for 18 hours. The reaction mixture was extracted with methylene chloride. Solvent was distilled off, and the acid was isolated by freezing it out. The product was 12.1 g (41%) of 3,3,3-trifluoro-2-(trifluoromethyl) propionic acid, obtained in the form of colorless crystals, m.p. 49.5-50.5° (from heptane) and b.p. 124-126° (750 mm)(with slight decomposition). The neutralization equivalent was 195.5, 194.5, the theoretical equivalent for $C_4F_6H_2O_2$ being 196.0. The acid chloride was prepared in the usual way with the aid of phosphorus pentachloride: yield 64%; b.p. 57-59° (752 mm); n_D^{20} 1.3086; d_4^{20} 1.5492; Found MR 26.56; Calculated for C_4F_6HOCl MR 26.66. Amide m.p. 154-155.5° (from benzene). Anilide m.p. 166.5-167.5° (from benzene).

Reactions of Ethyl 1,3,3,3-Tetrafluoro-2-(trifluoromethyl) propenyl Ether with Amines

Reaction with Aniline. A mixture of 4.5 g (0.02 mole) of ethyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether and 3.7 g (0.04 mole) of aniline was shaken and heated until mutual solution occurred. The crystalline mass formed on cooling was washed with dilute hydrochloric acid and with water. The product, amounting to 2.5 g (45%), was 3,3,3-trifluoro-2-(trifluoromethyl) propionanilide, m.p. 168-169° (from aqueous alcohol). In admixture with a sample obtained from the acid chloride and aniline there was no depression of melting point.

Found %: C 44.45; H 2.66; F 42.14; N 5.33 $C_{10}F_6H_7NO$. Calculated %: C 44.28; H 2.58; F 42.06; N 5.17.

Reaction with Diethylamine. A mixture of 11.3 g (0.05 mole) of ethyl 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propenyl ether and 15 ml of absolute ether was prepared in a flask fitted with stirrer, reflux condenser, and dropping funnel and protected from access of atmospheric moisture and carbon dioxide. The mixture was stirred and cooled with ice water, and 8 g (0.11 mole) of pure diethylamine was added over a period of one hour. The precipitate of diethylamine hydrochloride was filtered off, ether was distilled off, and the residue was distilled under reduced pressure. The product, amounting to 11.7 g (84.5%), was 1-ethoxy-N,N-diethyl-3,3,3-trifluoro-2-(trifluoromethyl) propenylamine, b.p. 68-71° (2 mm) and, after redistillation, b.p. 71° (2 mm); n_D^{20} 1.4071; d_4^{20} 1.2407; Found MR 55.10; Calculated for $C_{10}F_6H_{16}NO$ MR 54.34. Hydrolysis of 1-ethoxy-N,N-diethyl-3,3,3-trifluoro-2-(trifluoromethyl) propenylamine with dilute hydrochloric acid at 100° gave N,N-diethyl-3,3,3-trifluoro-2-(trifluoromethyl) propionamide, which melted without depression (m.p. 51-52°) in admixture with the product obtained from perfluoroisobutene and diethylamine.

The reaction of perfluoropropene with methanol was carried out in accordance with the previously described procedure [1]. The constants of 1,1,2,3,3,3-hexafluoropropyl methyl ether were: b.p. 54-55° (750 mm); n_D^{20} 1.2840; d_4^{20} 1.4185; Found MR 22.89: Calculated for $C_4F_6H_4O$ MR 23.15. (the literature [1] gives b. p. 54-55° (750 mm); d_4^{20} 1.429; n_D^{20} 1.2850) The dibromide (1,2-dibromo-1,2,3,3,3-pentafluoropropyl methyl ether) had b.p. 128-132° (732 mm); n_D^{20} 1.3871; d_4^{20} 1.9374; Found MR 39.19;: Calculated for $C_4F_6H_5Br_2O$ MR 38.54. (the literature [1] gives: b.p. 136°; d_4^{20} 1.900; n_D^{20} 1.3700).

1,1,2,3,3,3-Hexafluoropropyl methyl ether was converted by the method described into methyl 2,3,3,3-tetrafluoropropionate, b.p. 94° (750 mm) and n_D^{20} 1.3198 (the literature [1] gives b.p. 96° and n_D^{20} 1.3192.

2,3,3,3-Tetrafluoropropionamide. A mixture of 2.9 g of methyl 2,3,3,3-tetrafluoropropionate and 4 ml of concentrated aqueous ammonia was shaken until the oil had completely dissolved. The solution was evaporated at room temperature, and the residue was vacuum-dried. The product, amounting to 2.6 g (96%), was 2,3,3,3-tetrafluoropropionamide, m.p. 53.5-55.5°, raised by recrystallization from benzene to 58-59°.

Found %: C 24.75; H 2.11; F 52.25; N 9.56 $C_3F_4H_3NO$. Calculated %: C 24.84; H 2.09; F 52.41; N 9.66.

2,3,3,3-Tetrafluoropropionitrile. The dehydration of 7.2 g (0.05 mole) of 2,3,3,3-tetrafluoropropionamide gave 5.1 g (80.3%) of 2,3,3,3-tetrafluoropropionitrile, b.p. 41.5-42.5° (746 mm); n_D^{20} 1.27; d_4^{20} 1.3600.

Found %: C 28.58; H 0.84 C_3F_4HN. Calculated %: C 28.35; H 0.79

Hydrolysis of 1,2-Dibromo-1,2,3,3,3-pentafluoropropyl Methyl Ether. A mixture of 7.6 g (0.024 mole) of the dibromide, 2 ml of concentrated sulfuric acid (sp. gr. 1.82), and 2 g of finely ground glass was heated in a water bath for five hours. The reaction mixture was then decomposed by ice, washed with sodium bisulfite solution, and extracted with ether. The ether solution was washed with sodium bicarbonate solution and with water, and was dried over magnesium sulfate. Removal of ether gave a residue of 3.1 g (56%) of methyl 2-bromo-2,3,3-3-tetrafluoropropionate, b.p. 105-107° and n_D^{20} 1.3620. Redistillation gave a substance of b.p. 106-106.5° (733 mm); n_D^{20} 1.3617; d_4^{20} 1.6257; Found MR 31.06; Calculated for $C_4F_4H_3BrO_2$ MR 30.65.

Found %: Br 33.08; F 31.64 $C_4F_4H_3BrO_2$. Calculated %: Br 33.44; F 31.80.

Treatment of this ester with concentrated aqueous ammonia gave 2-bromo-2,3,3,3-tetrafluoropropionamide, m.p. 90-90.5° (from heptane).

Found %: Br 35.53; N 6.17 $C_3F_4H_3BrNO$. Calculated %: Br 35.68; N 6.28.

Reaction of Perfluoroisobutene with Amines

Reaction with Diethylamine. Dry perfluoroisobutene (26 g, i.e., 0.13 mole) was introduced over a period of 2.5 hours into a vigorously stirred, cooled (0°) solution of 20 g (0.27 mole) of dry diethylamine in 75 ml of absolute ether. When addition was complete, the mixture was left at room temperature for a further 30 minutes and then filtered from the precipitate of diethylamine hydrofluoride (11.6 g, i.e., 0.125 mole). The filtrate was left overnight in a refrigerator. After removal of ether and two fractionations, 16.5 g (65%) of N,N-diethyl-1,-3,3,3-tetrafluoro-2-(trifluoromethyl) propenylamine was obtained as a colorless liquid of characteristic pungent odor. It did not react with a solution of bromine in methylene chloride and hydrolyzed when exposed to the air for a short time; b.p. 66.5-67° (10 mm); n_D^{20} 1.3810; d_4^{20} 1.3256; Found MR 44.31; Calculated for $C_8F_7H_{10}N$ MR 43.60.

Found %: C 38.0; H 3.98; F 52.71; N 5.53 $C_8F_7H_{10}N$. Calculated %: C 37.95; H 3.98; F 52.53; N 5.53.

Hydrolysis of N,N-Diethyl-1,3,3,3-tetrafluoro-2-(trifluoromethyl)-propenylamine. A mixture of 7.1 g (0.028 mole) of the amine and 50 ml of water was stirred vigorously for 14 hours. The crystals formed in the flask were filtered off and washed with water. The product amounting to 6.0 g (85%), was N,N-diethyl-3,3,3-trifluoro-2-(trifluoromethyl) propionamide, m.p. 51-51.5° (from heptane).

Found %: C 38.43; H 4.41; F 45.48; N 5.32 $C_8F_6H_{11}ON$. Calculated %: C 38.25; H 4.013; F 45.42; N 5.57.

Reaction of Perfluoroisobutene with Aniline. A stream of perfluoroisobutene was passed into a vigorously stirred solution of 11 g (0.12 mole) of aniline in 50 ml of ether. The precipitate of aniline hydrofluoride was filtered off, ether was distilled off, and the residue was treated with cold dilute hydrochloric acid and with water; it was dried over magnesium sulfate. Fractionation gave 11.8 g of a substance of b.p. 77-79° (28 mm), n_D^{20}

1.4148; d_4^{20} 1.3869; Found MR 49.26; Calculated for $C_{10}F_7H_9N$ MR 49.97.

Found %: C 43.93; H 2.23; N 5.24 $C_{10}F_7H_9N$. Calculated %: C 43.98; H 2.21; N 5.13.

When treated with concentrated sulfuric acid, the substance of b.p 77-79° (28 mm) gave 3,3,3-trifluoro-2-(trifluoromethyl) propionanilide, m.p. 168.5-169° (from dilute alcohol). There was no depression of melting point in a mixture test with the sample described above.

Reaction of Perfluoropropene with Diethylamine

Dry perfluoropropene (37 g, i.e., 0.245 mole) was passed for two hours into a vigorously stirred solution of 40 g (0.55 mole) of dry diethylamine in 70 ml of absolute ether. When addition was complete, diethylamine hydrofluoride (12 g, i.e., 0.13 mole) was filtered off, ether was distilled off, and the residue was vacuum-distilled. The bulk of the material (32 g) came over at 52-52.5° (55 mm) (n_D^{20} 1.3550; d_4^{20} 1.2279*) and was found to be a mixture of N,N-diethylpentafluoropropenylamine and N,N-diethyl-1,1,2,3,3,3-hexafluoropropylamine. This mixture decomposed very readily in presence of air, reacted with a solution of bromine in methylene chloride, and was readily hydrolyzed by water with formation of N, N-diethyl-2,3,3,3-tetrafluoropropionamide as sole product: b.p. 89-90° (22 mm); n_D^{20} 1.3910 (the literature [1] gives b.p. 89° (22 mm); n_D^{20} 1.3910).

Reaction of Perfluoroisobutene with Ammonia

A solution of 25 g (0.125 mole) of perfluoroisobutene in 100 ml of absolute ether was cooled to −60° and stirred vigorously during the passage of 6 g (0.353 mole) of dry ammonia over a period of 2.5 hours. The temperature of the mixture was then allowed to rise to 0°, 20 ml of water was added, and stirring was continued for a further 1.5 hours. The reaction mixture was then washed, first with water, then with sodium bicarbonate solutions, and again with water; it was dried with magnesium sulfate. Fractionation gave 4.7 g (21%) of 3,3,3-trifluoro-2-(trifluoromethyl) propionitrile, b.p. 64-65° (750 mm); n_D^{20} 1.27; d_4^{20} 1.4560. From the residue in the flask, 2.5 g (13%) of 3,3,3-trifluoro-2-(trifluoromethyl) propionamide, m.p. 154.5-155° (from benzene), was isolated. The same compound was obtained by the action of alcoholic hydrogen chloride on 3,3,3-trifluoro-2-(trifluoromethyl) propionitrile and subsequent treatment with water; it melted at 154.5-155° (from benzene).

Found %: C 24.69; H 1.59; F 58.47 $C_4F_6H_5NO$. Calculated %: C 24.63; H 1.55; F 58.44.

Neither of these substances showed any depression of melting point in admixture with samples prepared from 3,3,3-trifluoro-2-(trifluoromethyl) propionyl chloride and ammonia.

Reaction of Perfluoropropene with Ammonia

Perfluoropropene (63 g, i.e., 0.42 mole) was passed into a cooled stirred mixture of 100 ml of dioxane and 20 ml of 30% aqueous ammonia. During the reaction, 30% ammonia (three 10-ml portions) was added periodically. When the introduction of perfluoropropene was complete, the reaction mixture was rapidly distilled into a well cooled receiver. The 38-95° fraction was poured into water, and the layer that separated was carefully washed free from dioxane with cold water and was dried over calcium chloride. Fractionation gave 23.8g (46.5%) of 2,3,3,3-tetrafluoropropionitrile, b.p. 40-41° (750 mm); n_D^{20} 1.27; d_4^{20} 1.3620.

Treatment of 2,3,3,3-tetrafluoropropionitrile with alcoholic hydrogen chloride and subsequent treatment with water gave ethyl 2,3,3,3-tetrafluoropropionate, which was converted by treatment with aqueous ammonia into 2,3,3,3-tetrafluoropropionamide, m.p. 58-59°. In admixture with the sample described above it melted without depression.

SUMMARY

1. It was shown that, when perfluoroisobutene and perfluoropropene react with alcohols and amines, not only addition occurs, but also replacement of the vinylic fluorine atom.

* The specific gravity and refractive index varied from one experiment to another. The results of elementary analysis were intermediate between those required for N,N-diethylpentafluoropropenylamine and those required for N,N-diethyl-1,1,2,3,3,3-hexafluoropropylamine.

2. The addition and substitution products so obtained were submitted to various reactions with formation of various derivatives of 3,3,3-trifluoro-2-(trifluoromethyl) propionic and 2,3,3,3-tetrafluoropropionic acids.

3. It was found that, with ammonia, perfluoroisobutene and perfluoropropene give 3,3,3-trifluoro-2-(trifluoromethyl) propionitrile and 2,3,3,3-tetrafluoropropionitrile, respectively.

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STRUCTURE OF COMPOUNDS FORMED FROM THIOPHENE AND 2-METHYLTHIOPHENE UNDER THE CONDITIONS OF CHLOROMETHYLATION IN PRESENCE OF ZINC CHLORIDE

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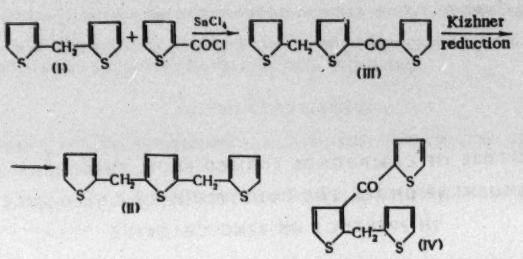
According to Blicke and Burckhalter [1], in the chloromethylation of thiophene with 40% formaldehyde and hydrochloric acid, not only 2-(chloromethyl) thiophene, but also 2,2'-methylenedithiophene (MDT) (I) is formed. The latter compound is obtained, though here as the main reaction product, also by reaction of thiophene with trioxane in presence of hydrofluoric acid [2]; in the reaction mixture obtained under these conditions a small amount of a compound of composition $C_{14}H_{12}S_3$ can be isolated, and this is assigned [2] the structure of 2,5-di-2-thienylthiophene (DTT) (II). 2,2'-Methylenedithiophene is obtained in higher yield by the condensation of 2-(chloromethyl) thiophene with 2-thienyllithium [3].

2,2'-Methylenedithiophene and 2,5-di-2-thenylthiophene are of interest as starting materials for the preparation of aliphatic compounds having a long carbon chain [4]. A simple method for the synthesis of MDT is described in the present paper; it is based on observations of Lock, who used zinc chloride as a condensing agent in the chloromethylation of benzene [5]. In presence of zinc chloride and hydrochloric acid, thiophene reacts with 35-37% formaldehyde solution at from −7° to 0° with formation of MDT in 50-55% yield. That the compound formed under these conditions is indeed 2,2'-methylenedithiophene (I) is shown by the fact that, when formylated with N-methylformanilide in presence of phosphoryl chloride, it gives 5-(2-thenyl)-2-thiophenecarboxaldehyde, which can be converted into n-decyl alcohol by the action of Raney nickel. It is further confirmed by the fact that a mixture of the compound with the MDT obtained (see experimental part) by reduction of di-2-thienyl ketone [6] by a modified Kizhner method [7] melts without depression.

Apart from MDT, in our experiments we obtained a mixture of high-boiling products, from which, as in the work with hydrofluoric acid (see above), we isolated a compound of composition $C_{14}H_{12}S_3$, m.p. 37.5-38.5°. From the way in which it was formed it was possible to assign the compound the structure (II), but not as the only one permissible, as it was impossible to exclude the possibility of isomerization, associated with migration of the thenyl radical from the α- to the β-position. Moreover, it must be remembered that in MDT (I) which is probably an intermediate product in the formation of the substance of m.p. 37.5-38.5°, the β-position is activated by the thenyl radical attached to the α-carbon atom of the ring. All this applies equally to the compound described as DTT (II) by Cairns, McKusick, and Weinmayr [2], who assumed this structure without giving any data in its support.

As the most probable structure for the substance of m.p. 37.5-38.5° is II (DTT), we decided to prepare it as follows, for comparison:

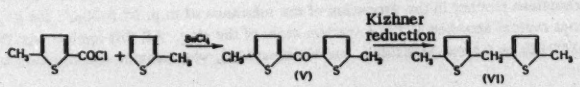


The ketone (III) is obtained in very low yield (10-12%). Attempts to improve the yield by the use of various condensing agents, change in the medium and the amount of stannic chloride, variations in the order of mixing the reactants, and alteration of temperature were not successful. Experiments on the acylation of MDT with 2-thiophenecarboxylic acid in presence of phosphoric oxide were also unsuccessful: under these conditions the anhydride of the thiophenecarboxylic acid was obtained instead of the expected ketone.

Of the two possible structures of the ketone, (III) and (IV), the second is not very probable, since, according to Hartough and Kosak [8], in the acylation of 2-alkylthiophenes, substitution of the acyl group in the 3-position does not occur to an appreciable extent. Reduction of the ketone (III) gave DTT (II), m.p. 37.5-38°, undepressed by admixture of the above-mentioned substance of composition $C_{14}H_{12}S_3$, isolated together with MDT in the chloromethylation of thiophene in presence of zinc chloride. The two dibromo derivatives, obtained from the reduction product of the ketone (III) and from the substance of m.p. 37.5-38.5°, were also found to be identical. These dibromo derivatives probably have the structure 2,5-bis(5-bromo-2-thenyl) thiophene.

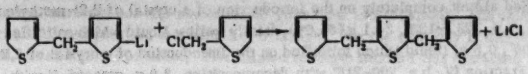
It may, therefore, be considered as established that, under our chosen conditions of chloromethylation, the process proceeds mainly in the direction of the formation of 2- and 2,5-substituted thiophenes of structures (I) and (II). On hydrogenolysis in presence of Raney nickel, the DTT that we isolated from the mixture gave the hydrocarbon $C_{14}H_{30}$, which was identical in properties with n-tetradecane.

Under the above-described conditions, 2-methylthiophene gave a 60-66% yield of a compound of composition $C_{11}H_{12}S_2$, m.p. 38.5-39.5°, together with a high-boiling mixture of products that we did not investigate more closely. In this case also – owing to the presence of an activating group (methyl) in the original alkylthiophene and owing to other causes (see above) – the formation of structures other than (VI) must be admitted as a possibility. However, after synthesizing 2,2'-methylene bis[5-methylthiophene] (VI) according to the scheme:



we convinced ourselves that this is identical with the compound of m.p. 38.5-39.5° mentioned above. Hence, under the given chloromethylation conditions, 2-methylthiophene reacts like thiophene, i.e., mainly in the free α-position. As we have stated, (II) and (VI) can be obtained by Kizhner reduction of the corresponding ketones. The yields of reduction products are quite satisfactory (50-65%). In view of these results, it became clear to us that the statement of the Swedish investigators Lofgren and Tegner [3] to the effect that di-2-thienyl ketone cannot be reduced by the Kizhner method is in error. Actually, in the reduction of this ketone, as also in the reduction of the ketones (III) and (V), we observed no departure from the usual course of reaction and obtained MDT in 65% yield.

The above-described method of synthesizing DTT, which consists in the reduction of the ketone (III) and was used by us as a method of proving the structure of the substance $C_{14}H_{12}S_3$, is not suitable as a method of preparing DTT owing to the fact that the ketone (III) is obtained in low yield. A more suitable method of preparing 2,4-di-2-thenylthiophene consists in the condensation of 2-(chloromethyl) thiophene with the lithium derivative of 2,2'-methylenedithiophene [4]:



Under these conditions DTT is obtained in 47% yield, calculated on the amount of 2,2'-methylenedithiophene that reacted.

EXPERIMENTAL

Reaction of Thiophene with Formaldehyde in presence of Hydrochloric Acid and Zinc Chloride. Hydrochloric acid (82 ml, sp. gr. 1.19) was cooled to −10° and stirred while 108 g (0.78 mole) of anhydrous zinc chloride was added in small portions. When the zinc chloride had dissolved, 100.8 g (1.2 mole) of thiophene was added, and the mixture was stirred at from −7° to 0° while 75 g (0.9 mole) of 37% formaldehyde solution was added dropwise over a period of 1.5-1.75 hours; stirring at this temperature was continued for a further period of one hour.* After being shaken with 150 ml of water, the reaction mixture was extracted with ether; some yellowish-brown resin then separated (about 1 g).** The extract was washed with water, with saturated sodium bicarbonate solution, and again with water. It was dried over calcium chloride, and solvent was distilled off. Vacuum fractionation of the residue gave: Fraction I, b.p. 129-135° (10 mm), 56.3 g, a liquid which solidified after being distilled; Fraction II, b.p. 130-185° (3 mm), 0.8 g, a lemon-yellow liquid; Fraction III, distilling with slight decomposition at 185-240° (3 mm), 16.5 g, n_D^{20} 1.6348, a yellow liquid that thickened after long standing; 24.2 g of residue, a very viscous liquid.

After redistillation Fraction I boiled at 131-133° (11 mm), 54.2 g (50.2%) of 2,2'-methylenedithiophene, m.p. 44.5-46.5° (from alcohol and petroleum ether) being obtained. In some cases the yield of nonrecrystallized product attained 55%. There was no depression of melting point in a mixture test with 2,2'-methylenedithiophene prepared by the reduction of di-2-thienyl ketone (see below).

Found %: C 59.95; 60.24; H 4.55; 4.59; S 35.27; 35.43 $C_9H_8S_2$. Calculated %: C 60.00; H 4.44; S 35.55

After redistillation Fraction III boiled at 184-187° (2 mm), 12.5 g (about 11%) of 2,5-di-2-thenylthiophene being obtained as a yellow oil (n_D^{20} 1.6344) which crystallized when allowed to stand. Recrystallization – from a mixture of butyl alcohol and acetone or of methanol and acetone and then from petroleum ether – gave 2,5-di-2-thenylthiophene in the form of colorless crystals, m.p. 37.5-38.5°.

Found %: C 60.87; 61.13; H 4.36; 4.44; S 34.72; 34.72 $C_{14}H_{12}S_3$. Calculated %: C 60.86; H 4.35; S 34.78
Found: M 271.4 Calculated: M 276.43

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* Sometimes the reaction mixture solidifies after 10-20 minutes, in which case stirring is stopped.

** When formaldehyde is added rapidly, the temperature of the mixture rises above 0°. The yield of 2,2'-methylenedithiophene is then reduced and the amount of resin formed is increased with formation of difficultly separable suspensions. In this case, the suspension is separated from the aqueous layer, ether is added, and the mixture is shaken; the resin then partially coagulates. The extract is decanted from the settled resin into a separating funnel, ether is again added, and the ether extract is again separated. This procedure is repeated several times.

In admixture with the reduction product from 5-(2-thenyl)-2-thienyl-2-thienyl ketone, this substance showed no depression of melting point.

2,2'-Methylenebis [5-methylthiophene]. The product obtained under the above-described conditions from 34 ml of concentrated hydrochloric acid, 49 g (0.5 mole) of 2-methylthiophene, and 31.2 g (0.386 mole) of 37% formaldehyde solution in presence of 48 g (0.35 mole) of zinc chloride was suitably treated and then distilled at 3 mm. The following fractions were obtained: Fraction I, boiling up to 128.5°, 0.6 g, colorless liquid which solidified almost completely on the introduction of a crystal of 2,2'-methylenebis [5-methylthiophene]; Fraction II, b.p. 128.5-133°, 34.1 g (65.6%), faintly yellow liquid which solidified on standing; Fraction III, b.p. 133-200°, 0.5 g, liquid which solidified on the introduction of a crystal of 2,2'-methylenebis [5-methylthiophene]; Fraction IV, b.p. 200-215° with decomposition, 3.6 g, greenish liquid; residue, 8.7 g, colored vitreous mass. When redistilled, Fraction II boiled at 116-118° (2 mm) and gave 31 g (60%) of a colorless liquid which solidified on standing.

After recrystallization from alcohol 2,2'-methylenebis[5-methylthiophene] had m.p. 38.5-39.5°, undepressed by admixture of the reduction product from bis(5-methyl-2-thienyl) ketone (see below) or of 2,2'-methylenebis [5-methylthiophene] prepared by the method of Emerson and Patrick [9].

Found %: C 63.61; 63.44; H 5.68; 5.76; S 30.84; 30.56 $C_{11}H_{12}S_2$. Calculated %: C 63.44; H 5.77; S 30.77.

Reduction of Di-2-thienyl Ketone. A mixture of 5.82 g (0.03 mole) of di-2-thienyl ketone, 55 ml of diethylene glycol, and 4.5 ml (0.09 mole) of 99% hydrazine hydrate was heated under reflux to 130°. The mixture was cooled, and 6 g (0.10 mole) of potassium hydroxide was added. It was then refluxed for one hour. Water and excess of hydrazine hydrate were then distilled off at 195-200°, and the mixture was again refluxed for three hours. The cooled solution was diluted with 75 ml of water and extracted with ether. This extract was combined with an extract of the aqueous distillate (see above). The extract was shaken with 6 N HCl, with water, with 10% sodium carbonate solution, and again with water; it was then dried over calcium chloride. Solvent was distilled off, and vacuum distillation of the residue gave 3.5 g (65%) of crude di-2-thienyl ketone, b.p. 133-135.5° (12 mm); after recrystallization from alcohol and petroleum ether it melted at 46-47.5°. A mixture of this substance with di-2-thienyl ketone prepared by reaction of thiophene with formaldehyde in presence of hydrochloric acid and zinc chloride melted at 45-47°.

Found %: C 60.00; 60.20; H 4.48; 4.33; S 35.80; 36.09 $C_9H_6S_2$. Calculated %: C 60.00; H 4.44; S 35.55

Reduction of Bis(5-methyl-2-thienyl) Ketone to 2,2'-Methylenebis[5-methylthiophene]. The product obtained by boiling a mixture of 5.55 g of bis(5-methyl-2-thienyl) ketone, 5.6 g of potassium hydroxide, 60 ml of diethylene glycol, and 5 ml of 99% hydrazine hydrate was treated as in the preceding experiment and fractionated at 5 mm. The product, amounting to 3.2 g (62%), was bis(5-methyl-2-thienyl) ketone b.p. 128.5-132°, m.p. 38.5-39.5° (from alcohol).

Found %: C 63.34; 63.23; H 5.74; 5.82; S 30.90; 30.97 $C_{11}H_{12}S_2$. Calculated %: C 63.43; H 5.77; S 30.77.

A mixture of this substance with the bis(5-methyl-2-thienyl) ketone obtained by reaction of 2-methylthiophene with formaldehyde in presence of hydrochloric acid and zinc chloride melted at the same temperature.

Reduction of 5-(2-Thenyl)-2-Thienyl-2-Thienyl Ketone to 2,5-Di-2-thenylthiophene. The product obtained by the action of 1 ml of 99% hydrazine hydrate on 1.5 g of 5-(2-thenyl)-2-thienyl 2-thienyl ketone in 16 ml of diethylene glycol in presence of 1 g of potassium hydroxide was distilled at 3 mm. The product, amounting to 0.72 g (50.5%), was 2,5-di-2-thenylthiophene, b.p. 192-195°, m.p. 37.5-38° (from butyl alcohol).

Found %: C 61.07; 61.28; H 4.23; 4.36; S 34.84; 34.64 $C_{14}H_{12}S_3$. Calculated %: C 60.86; H 4.35 S 34.78.

In admixture with the 2,5-di-2-thenylthiophene obtained in the chloromethylation of thiophene in presence of zinc chloride there was no depression of melting point.

Synthesis of 5-(2-thenyl)-2-thiophenecarboxaldehyde. A mixture of 31.6 g (0.234 mole) of freshly distilled N-methylformanilide and 35.92 g (0.234 mole) of phosphoryl chloride was prepared in a four-necked flask fitted with mercury-sealed stirrer, thermometer, dropping funnel, and calcium chloride tube. After 30 minutes a solution of 32.4 g (0.18 mole) of 2,2'-methylenedithiophene in 40 ml of dry toluene was added at such a rate that the temperature did not rise above 25-35° (one hour was required). The mixture was stirred for a further two hours at this temperature and then left overnight. On the next day it was poured into a mixture of 85 g of crushed ice and 95 ml of water. The diluted reaction mixture was extracted with three 200 ml portions of ether and with one 75 ml portion of toluene. The ether-toluene extract was washed three times with 10% hydrochloric acid solution, several times with saturated sodium bicarbonate solution, and with water. It was dried over calcined magnesium sulfate, and solvent was distilled off. The residue — a dark-red liquid — was vacuum-distilled. The following fractions were obtained: Fraction I, b.p. 122-152° (11 mm), 8 g, a liquid that solidified when a crystal of 2,2'-methylenedithiophene was introduced; Fraction II, b.p. 135-157° (3 mm), 1.1 g, a liquid which did not crystallize when 2, 2'-methylenedithiophene was added; Fraction III, b.p. 158-162° (3 mm), 19 g, n_D^{20} 1.6425, a red oil. A residue of 4.7 g of resin remained in the flask.

Refractionation of Fraction III gave 18 g of oil, b.p. 156-159° (3 mm), n_D^{20} 1.6422, which solidified on standing. Recrystallization from absolute methanol gave 5-(2-thenyl)-2-thiophenecarboxaldehyde, m.p. 33-34°.

Found %: C 58.07; 58.09; H 3.94; 3.74; S 30.86; 30.64 $C_{10}H_8OS_2$. Calculated %: C 57.69; H 3.84; S 30.77.

A mixture of Fractions I and II was again vacuum-fractionated, and 7.3 g (22.5%) of unchanged 2,2'-methylenedithiophene, b.p. 122-130° (10 mm), was obtained. The yield of 5-(2-thenyl)-2-thiophencarboxaldehyde was 48% on the original amount of 2,2'-methylenedithiophene and 63% on the amount that reacted. After recrystallization from alcohol, the semicarbazone of this aldehyde melted at 207-209°.

Found %: N 15.90; 15.77 $C_{11}H_{11}ON_3S_2$. Calculated %: N 15.85.

The oxime melted at 93.5-95° (from dilute alcohol).

Found %: N 6.21; 6.09 $C_{10}H_9ONS_2$. Calculated %: N 6.28.

Preparation of 5-(2-Thenyl)-2-thienyl 2-Thienyl Ketone. A solution of 12.6 g (0.07 mole) of 2,2'-methylenedithiophene in 150 ml of benzene and 10.3 g (0.07 mole) of 2-thiophenecarbonyl chloride were mixed in a four-necked flask fitted with mercury-sealed stirrer, reflux condenser fitted with calcium chloride tube, thermometer, and dropping funnel. The mixture was stirred at 0° for 30 minutes while 18.2 g (0.07 mole) of stannic chloride was added dropwise. The mixture became dark in color and resin appeared on the walls of the vessel. Stirring was continued for a further one hour at room temperature, and 150 ml of 10% aqueous hydrochloric acid was then added. After stirring for three hours and removal of the liquid part, the residual resin was repeatedly shaken and heated with new portions of benzene and hydrochloric acid, but the amount of the resin did not diminish appreciably. The benzene extracts were combined and washed with water, with saturated sodium bicarbonate solution, and again with water. They were dried over calcium chloride, the solvent was distilled off, and the residue was fractionated at 3 mm. The following fractions were obtained: Fraction I, b.p. 101-102°, 1 g, a liquid that solidified when some 2,2'-methylenedithiophene was added; Fraction II, b.p. 232-235°, 2.4 g, a yellow oil that solidified in the receiver; residue, 8.3 g of resin.

Fraction II, after repeated recrystallization from methanol and ethanol, melted at 104.5-105.5°.

Found %: C 57.92; 57.81; H 3.27; 3.31 $C_{14}H_{10}OS_3$. Calculated %: C 57.93; H 3.44.

Found: M 281.5 (cryoscopically)
Calculated: M 290.

The yield of crude 5-(2-thenyl)-2-thienyl 2-thienyl ketone was about 12%.

Reductive Desulfurization of 5-(2-Thenyl)-2-thiophenecarboxaldehyde. Preparation of n-Decyl Alcohol. A mixture of 10.4 g (0.05 mole) of 5-(2-thenyl)-2-thiophenecarboxaldehyde, 750 ml of ethanol, and 100 g of Raney nickel* was stirred under reflux for 3.5 hours in a boiling water bath. The mixture was allowed to settle for 16 hours, and the alcoholic solution was decanted and the catalyst was treated three times with stirring with 200 ml portions of hot ethanol. The catalyst was filtered off. Alcohol was distilled from the alcoholic solution, and about 150 ml of water was added to the residue. The mixture was extracted with chloroform, and the extract was dried over magnesium sulfate. The residue was vacuum-distilled: Fraction I, b.p. 115-117° (13-14 mm) 3.2 g (35.4%), colorless pleasantly smelling liquid, which solidified when cooled strongly; n_D^{20} 1.4380, d_4^{20} 0.8328; Found MR 49.87; Calculated MR 49.90.

Found %: C 75.91; 75.70; H 13.72; 13.59. $C_{10}H_{22}O$. Calculated %: C 75.96; H 13.98.

The residue, 1.2 g, was a viscous mass.

After recrystallization from 95% ethanol, the phenylurethane obtained from Fraction I melted at 58.5-59.5°.

Found %: C 73.41; 73.67; H 9.78; 9.87; N 5.13; 5.31 $C_{17}H_{27}O_2N$. Calculated %: C 73.65; H 9.74; N 5.05.

There was no depression of melting point in admixture with the phenylurethane of a known sample of decyl alcohol. According to the literature [11], this urethane melts at 59.6°.

Reduction Desulfurization of 2,5-Di-2-thenylthiophene. Preparation of n-Tetradecane. The hydrogenolysis product obtained from 9.66 g (0.035 mole) of unrecrystallized 2,5-di-2-thenylthiophene, 100 g of Raney nickel, and 750 ml of ethanol was vacuum-fractionated: Fraction I, b.p. 114-118° (10 mm), 4.1 g (59.2%), n_D^{20} 1.4310, colorless liquid that solidified when cooled strongly;

Found %: C 84.75; 85.01; H 15.13; 15.19 $C_{14}H_{30}$. Calculated %: C 84.85; H 15.15.

Fraction II, b.p. 185-205° (3 mm), 0.75 g, a yellow oil, which solidified in the side tube; residue in flask, 0.3 g, immobile yellow mass.

Redistillation of Fraction I gave:

Fraction Ia: b.p. 109-115° (11 mm); 0.67, n_D^{20} 1.4291.
Fraction Ib: b.p. 115-118° (11 mm) 3.1 g, n_D^{20} 1.4301, d_4^{20} 0.7646, Found MR 67.03; Calculated MR 66.85.

Recrystallization of Fraction II from alcohol gave a sulfur-free crystalline substance of indefinite melting point: it became "wet" at 45°, started to melt at 49.5°, and was completely melted at 57°.

Found %: C 85.38; 85.56; H 14.72; 14.72

This substance is probably a mixture of solid hydrocarbons of high molecular weight.

Bromination of 2,5-Di-2-thenylthiophene. A mixture of 8.28 g (0.03 mole) of 2,5-di-2-thenylthiophene obtained in the chloromethylation of thiophene (see above), 130 ml of benzene, and 130 ml of concentrated hydrochloric acid was cooled to 5-7°, and the mixture was stirred while 253 ml of 0.522 N bromide-bromate mixture was added dropwise over a period of about two hours. The mixture was stirred for three hours further at the same temperature, the organic layer was separated, and the aqueous part was extracted with benzene. The organic layer was combined with the extract and washed with water, with 10% sodium hydroxide solution, with saturated thiosulfate solution, and again with water; it was then allowed to stand over solid potassium hydroxide. The residue remaining after removal of solvent was a dark-colored hard resinous mass. It was boiled with alcohol in presence of activated charcoal. A yellowish crystalline substance was isolated from the

* The catalyst was prepared from 30% nickel-aluminum alloy by the method of Billica and Adkins [10], with the exception that the treatment with water was not carried out in a hydrogen atmosphere and the washing with alcohol was carried out without centrifugation.

alcoholic solution (6 g, i.e., 46%). After repeated recrystallization from alcohol it melted at 59-60°.

Found %: C 38.83; 39.00; H 2.24; 2.38 $C_{14}H_{10}Br_2S_3$. Calculated %: C 38.71; H 2.33.

Bromination of the Reduction Product of 5-(2-Thenyl)-2-Thienyl 2-Thienyl Ketone. This was carried out under the conditions described for the preceding experiment. Reaction was between 0.35 g of the reduction product in 6 ml of benzene, 6 ml of concentrated hydrochloric acid, and 10.4 ml of 0.5161 N bromide-bromate mixture. Recrystallization of the product from alcohol in presence of activated charcoal gave 0.08 g of crystals, m.p. 58-59°.

Found %: C 38.96; 38.84; H 2.36; 2.35 $C_{14}H_{10}Br_2S_3$. Calculated %: C 38.71; H 2.33.

A mixture test of this substance with the dibromo compound obtained from 2,5-di-2-thenylthiophene showed no depression of melting point.

Preparation of Bis(5-methyl-2-thienyl) Ketone [12]. A solution of 6.8 ml (0.0583 mole) of stannic chloride in 7 ml of benzene was added over a period of 40 minutes to a vigorously stirred cooled mixture of 9.4 g (0.0583 mole) of 5-methyl-2-thiophenecarbonyl chloride, 5.72 g (0.0583 mole) of 2 methylthiophene, and 60 ml of dry benzene at from −2° to 0°.

Stirring was continued for one hour without external cooling, and the mixture was treated with 10% aqueous hydrochloric acid. The aqueous layer was extracted with benzene. The benzene solution was washed with water and dried with calcium chloride. Benzene was distilled off, and the residue was vacuum-distilled. The product, amounting to 11.38 g (88%), was bis(5-methyl-2-thienyl) ketone, b.p. 212-214° (13 mm), m.p. 48-49° after recrystallization from dilute methanol (the literature [13] gives m.p. 53°).

Found %: C 59.63; 59.42; H 4.48; 4.46 $C_{11}H_{10}S_3$. Calculated %: C 59.46; H 4.5.

Preparation of 2,5-Di-2-thenylthiophene. The experiment was carried out in an atmosphere of nitrogen. Over a period of 40 minutes at from −3° to 0°, 153 ml of a 0.65 N ethereal solution of butyllithium (0.1 mole) was added to a solution of 22 g (0.122 mole) of 2,2'-methylenedithiophene in 160 ml of absolute methanol, precautions being taken to exclude atmospheric moisture. The contents of the flask were stirred for a further 20 minutes, and at from −2° to 0° 14.2 g (0.107 mole) of 2-(chloromethyl) thiophene in 60 ml of dry ether was added over a period of 70 minutes. After 15 hours at room temperature and six hours under reflux in a boiling water bath, the mixture was decomposed with 100 ml of water. The ethereal layer was separated, washed with water, and dried over calcium chloride. The residue after removal of ether was vacuum-fractionated. The following fractions were obtained: Fraction I, b.p. 60-120 (24 mm), 2.34 g, a yellow liquid of pungent odor; Fraction II, b.p. 95-190° (12-13 mm), 10.9 g, a yellow liquid that partially solidified on standing; Fraction III, b.p. 192-215° (4 mm), 12 g, yellowish-brown liquid that solidified when cooled; residue in flask, 6.64 g, reddish-brown viscous liquid.

Redistillation of Fraction II gave 7 g of unchanged 2,2'-methylenedithiophene, b.p. 128-135° (12 mm) and 0.82 g of 2,5-di-2-thenylthiophene, b.p. 188-193° (3 mm).

On redistillation Fraction III boiled at 188-192° (3 mm), and 10.07 g of 2,5-di-2-thenylthiophene was obtained as a yellowish oil that solidified on standing. The total yield of 2,5-di-2-thenylthiophene was 10.9 g (47% on the amount of 2,2'-methylenedithiophene that reacted). Recrystallization, first from a mixture of butyl alcohol and acetone and then from petroleum ether, gave colorless crystals, m.p. 37.2-38.2°.

Found %: C 60.78; 60.71; H 4.46; 4.46; S 34.65; 34.80 $C_{14}H_{12}S_3$. Calculated %: C 60.86; H 4.35; S 34.78.
Found: M 265
Calculated: M 276.43.

A mixture test of this product and the 2,5-di-2-thenylthiophene obtained in the chloromethylation of thiophene in presence of zinc chloride (see above) showed no depression of melting point (the mixture melted at 37.5-38.5°).

SUMMARY

1. Readily accessible methods for the preparation of 2,2'-methylenedithiophene and 2,2'-methylenebis-[5-methylthiophene] are described.

2. It is shown that the product of composition $C_{14}H_{12}S_3$ formed together with 2,2'-methylenedithiophene under the conditions of chloromethylation of thiophene is 2,5-di-2-thenylthiophene.

3. It is shown that, contrary to reports in the literature, di-2-thienyl ketone can be reduced by the Kizhner method.

4. By hydrogenolysis treatments, 2,5-di-2-thenylthiophene was converted into n-tetradecane and 5(2-thienyl)-2 thiophenecarboxaldehyde was converted into n-decyl alcohol.

5. A method was worked out for the preparation of 2,5-di-2-thenylthiophene.

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ACETYLENE DERIVATIVES

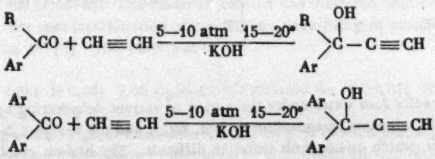
COMMUNICATION 177. CONDENSATION OF AROMATIC AND ALIPHATIC-AROMATIC KETONES WITH ACETYLENE UNDER PRESSURE. PART III.

I. N. Nazarov and V. F. Ryabchenko

In previous communications [1] we described a new method for the synthesis of acetylenic alcohols by the condensation of aldehydes and ketones with acetylene under pressure in presence of potassium hydroxide powder. Aldehydes and ketones of the most varied types can be condensed readily and rapidly with acetylene by this method, and in most cases the corresponding acetylenic alcohols are obtained in almost theoretical yield. It was of great interest to make use of this method for the preparation also of acetylenic alcohols containing aromatic radicals.

Attempts made by many investigators [2-4] to effect the condensation of acetylene with aromatic and aliphatic-aromatic ketones with the object of obtaining the corresponding acetylenic alcohols did not generally give satisfactory results, and these alcohols have remained very difficultly accessible. Condensation with acetylene at atmospheric pressure was carried out satisfactorily only for p-tolyl ketones, the corresponding acetylenic alcohols being obtained in yields of about 70% [5]. However, the development of a fairly simple method for the synthesis of various acetylenic alcohols containing aromatic radicals can be of great importance for the further development of acetylene-based organic synthesis. We therefore decided to make a careful investigation of the condensation of acetylene with aromatic and aliphatic-aromatic ketones by our method of reaction under a pressure of acetylene.

It was found that, in presence of potassium hydroxide powder at room temperature, aromatic and aliphatic-aromatic ketones of the benzo- and aceto-phenone types readily condense with acetylene under a pressure of 5-10 atm and give the corresponding tertiary acetylenic alcohols in yields of greater than 90%:



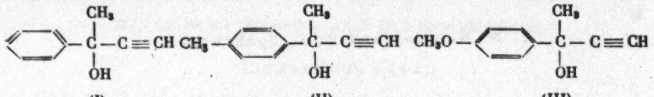
R = alkyl, Ar = aryl.

The success of these condensations depends not only on the use of acetylene under pressure, but also on the use of a considerable excess (2-3 molecular proportions) of potassium hydroxide and a long period (4-6 hours) of reaction. On the other hand, aliphatic, alicyclic, and heterocyclic ketones condense with acetylene under pressure rapidly and almost completely in presence of the equivalent amount of potassium hydroxide.

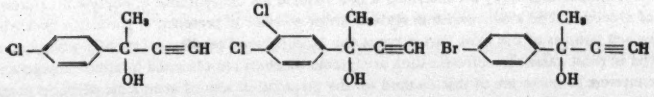
As already pointed out [1], the yield of acetylenic alcohol is improved appreciably by addition of a little aliphatic alcohol (ethanol) to the reaction mixture; the alcohol serves as a carrier of potassium ions in the organometallic mechanism of this condensation:

$$ROH + KOH \rightleftarrows ROK + H_2O;$$
$$ROK + CH \equiv CH \rightleftarrows CH \equiv CK + ROH.$$

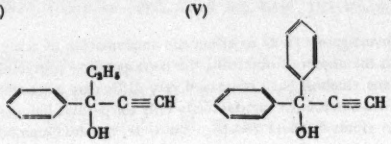
When condensation is not complete, the unchanged ketone can be recovered almost completely. The use of an excess of potassium hydroxide and acetylene under pressure increases the concentration of potassium acetylide in the reaction mixture and ensures that conditions exist for the completion of reaction. In this way we prepared the following acetylenic alcohols:



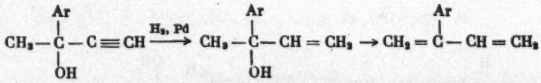
(I) (II) (III)



(IV) (V) (VI)



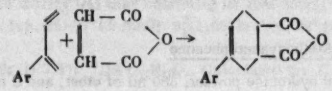
By the selective hydrogenation [6] of the resulting acetylenic alcohols in presence of a palladium catalyst almost quantitative yields of the corresponding ethylenic alcohols (IX) were obtained, and dehydration of these gave 2-aryl-1,3-butadienes (X):



2-Aryl-3-buten-2-ols readily lose water under the action of various dehydrating agents (potassium hydrogen sulfate, p-toluenesulfonic acid, alumina, magnesium sulfate, etc.), and the 2-aryl-1,3-butadienes then formed polymerize extremely readily, which makes their isolation difficult. The highest yield of 2-arylbutadienes (about 80%) was obtained by distillation of 2-aryl-3-buten-2-ols under reduced pressure in presence of a small amount of potassium hydrogen sulfate powder (0.1-1%) or by passage of the alcohols, diluted with water, over alumina at 240-280° under somewhat reduced pressure. In all cases it is desirable to carry out the dehydration in an atmosphere of nitrogen and to remove the 2-arylbutadienes as rapidly as possible from the reaction zone in order to avoid polymer (dimer) formation. Some dehydrating agents, e.g., p-toluenesulfonic acid, bring about rapid polymerization of 2-arylbutadienes and are, therefore, not suitable for the dehydration of 2-aryl-3-buten-2-ols.

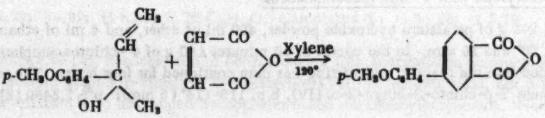
Of the 2-arylbutadienes that we investigated, 2-p-methoxyphenyl-1,3-butadiene polymerized most rapidly and was most difficult to prepare. The diene properties of 2-arylbutadienes are so marked that, even at room

temperature (during storage), they are fairly rapidly converted into dimers; they condense extremely readily with maleic anhydride with formation of the corresponding adducts (XI):



Ar = C_6H_5, p-$CH_3OC_6H_4$, p-ClC_6H_4.

Instead of the 2-arylbutadienes, the 2-aryl-3-buten-2-ols may be used directly in the diene condensation, but they may be dehydrated under the conditions of the reaction. For example, when 2-p-methoxyphenyl-3-buten-2-ol is treated with maleic anhydride in boiling xylene for 20-25 minutes, the corresponding adduct of 2-p-methoxyphenyl-1,3-butadiene is formed in 60% yield:



EXPERIMENTAL

Substituted acetophenones were prepared by the Friedel-Crafts reaction from the corresponding substituted benzenes and acetic anhydride in presence of aluminum chloride. The condensation of aliphatic-aromatic and aromatic ketones with acetylene under pressure was carried out in a steel reactor, as described in a previous communication [1].

Condensation of Acetylene with Acetophenone

A mixture of 470 g of potassium hydroxide powder, 15 ml of ethanol, and 1600 ml of dry ether was saturated with acetylene at 15° and 8 atm. In the course of 90 minutes 360 g of acetophenone was introduced into the reactor, and stirring of the reaction mixture under these conditions then continued for a further four hours. The pressure was released, and 900 ml of water was added to the reactor. The mixture was stirred carefully, and the aqueous alkaline layer was removed. The ethereal solution was saturated with carbon dioxide and dried with potassium carbonate. Vacuum fractionation of the product gave 398 g of pure 2-phenyl-3-butyn-2-ol (I), b.p. 82-83° (4 mm), m.p. 49° [7]. The yield was 91%.

Found %: C 82.00; 82.06; H 6.94; 7.05 $C_{10}H_{10}O$. Calculated %: C 82.05; H 6.85.

In this experiment, 5 g of the original acetophenone and 20 g of the acetylenic glycol were also isolated. This condensation was carried out in presence of sodamide by Carothers [2], who obtained 2-phenyl-3-butyn-2-ol (I) in a yield of only about 2%.

Condensation of Acetylene with 4'-Methylacetophenone

A mixture of 200 g of potassium hydroxide powder, 400 ml of ether, and 4 ml of ethanol was saturated with acetylene at 30° and 10 atm. In the course of 70 minutes 110 g of 4'-methylacetophenone in 100 ml of ether was introduced into the reactor, and stirring continued for a further five hours. The usual treatment gave 104 g of 2-p-tolyl-3-butyn-2-ol (II), b.p. 103-104° (4 mm); n_D^{20} 1.5304; d_4^{20} 1.0081; Found MR 49.03; Calculated MR 48.92.

Found %: C 82.42; 82.23; H 7.56; 7.61 $C_{11}H_{12}O$. Calculated %: C 82.50; H 7.50.

In addition, 3.4 g of the acetylenic glycol and 16 g of the original 4'-methylacetophenone were isolated. The yield of the acetylenic alcohol (II) was 80% of the amount of 4'-methylacetophenone taken and 93% on the amount that reacted. As Lebedev [5] showed, in the condensation of acetylene with 4'-methylacetophenone in presence of potassium hydroxide at atmospheric pressure, the acetylenic alcohol (II) is formed in only 5% yield.

Condensation of Acetylene with 4'-Methoxyacetophenone

A mixture of 200 g of potassium hydroxide powder, 350 ml of ether, and 3 ml of ethanol was saturated with acetylene at 25° and 10 atm. In the course of 80 minutes 110 g of 4'-methoxyacetophenone was introduced into the reactor, and stirring was then continued for four hours. The usual treatment gave 110 g (86%) of 2-p-methoxyphenyl-3-butyn-2-ol (III) b.p. 108-109° (1 mm), m.p. 35° (from petroleum ether), n_D^{20} 1.5440, d_4^{20} 1.0869, Found MR 50.81; Calculated MR 50.58.

Found %: C 74.76; 74.94; H 6.92; 6.93 $C_{11}H_{12}O_2$. Calculated %: C 75.00; H 6.87.

In addition, 1.6 g of the acetylenic alcohol was obtained.

Condensation of Acetylene with 4'-Chloroacetophenone

A mixture of 200 g of potassium hydroxide powder, 400 ml of ether, and 4 ml of ethanol was saturated with acetylene at 20° and 10 atm. In the course of 80 minutes 110 g of 4'-chloroacetophenone in 100 ml of ether was introduced into the reactor, and stirring was then continued for four hours. The usual treatment gave 122 g (95.5%) of pure 2-p-chloro-3-butyn-2-ol (IV), b.p. 113-114° (5 mm); n_D^{20} 1.5460 [8]; b.p. 43° (from isooctane).

Found %: C 65.50; 65.53; H 5.20; 5.23; Cl 19.53; 19.41 $C_{10}H_9OCl$. Calculated %: C 65.80; H 5.00; Cl 19.66.

Condensation of Acetylene with 3',4'-Dichloroacetophenone

A mixture of 180 g of potassium hydroxide powder, 400 ml of ether, and 4 ml of ethanol was saturated with acetylene at 25° and 10 atm. In the course of 80 minutes 95 g of 3',4'-dichloroacetophenone in 100 ml of ether was introduced into the reactor, and stirring was then continued for five hours. The usual treatment gave 98 g of 2-(3,4-dichlorophenyl)-3-butyn-2-ol (V), b.p. 122-123° (3 mm); n_D^{20} 1.5620; m.p. 112°.

Found %: C 55.86; 55.98; H 3.84; 3.78; Cl 32.98; 32.98 $C_{10}H_8OCl_2$. Calculated %: C 55.80; H 3.72; Cl 32.71.

In addition, 2 g of the acetylenic alcohol and 4.1 g of the original 3',4'-dichloroacetophenone were isolated. The yield of the acetylenic alcohol (V) was 91% on the amount of 3',4'-dichloroacetophenone taken and 96% on the amount that reacted.

Condensation of Acetylene with 4'-Bromoacetophenone

A mixture of 100 g of potassium hydroxide powder, 350 ml of ether, and 3 ml of ethanol was saturated with acetylene at 20° and 10 atm. In the course of 90 minutes 50 g of 4'-bromoacetophenone in 50 ml of ether was introduced into the reactor, and stirring was then continued for five hours. The product, amounting to 45 g, was 2-p-bromophenyl-3-butyn-2-ol (VI), b.p. 120-121° (3 mm); n_D^{20} 1.5720; m.p. 41-42° (from isoctane).

Found %: Br 35.95; 35.86; C 53.25; 53.12; H 4.02; 3.97 $C_{10}H_9OBr$. Calculated %: Br 35.56; C 53.33; H 4.00.

In addition, 0.8 g of the acetylenic glycol and 7 g of the original ketone were obtained. The yield of the acetylenic alcohol (VI) was 80% on the amount of 4'-bromoacetophenone taken and 92% on the amount that reacted.

Condensation of Acetylene with Propiophenone

A mixture of 200 g of potassium hydroxide powder, 400 ml of ether, and 4 ml of ethanol was saturated with acetylene at 25° and 10 atm. In the course of 80 minutes 120 g of propiophenone in 100 ml of ether was introduced into the reactor, and stirring was then continued for five hours. The usual treatment gave 122 g of 3-phenyl-1-pentyn-3-ol (VII), b.p. 86-87° (2 mm); n_D^{20} 1.5302; b.p. 34° [9].

Found %: C 82.57; 82.59; H 7.47; 7.54 $C_{11}H_{12}O$. Calculated %: C 82.50; H 7.50.

Also, 0.8 g of the acetylenic glycol and 5 g of the original propiophenone were obtained. The yield of the acetylenic alcohol (VII) was 85% on the amount of ketone taken and 89% on the amount that reacted.

Condensation of Acetylene with Benzophenone

A mixture of 120 g of potassium hydroxide powder, 250 ml of ether, and 5 ml of ethanol was saturated with acetylene at 10° and 9 atm. In the course of 85 minutes 91 g of benzophenone in 100 ml of ether was introduced into the reactor, and stirring was then continued for five hours. The usual treatment gave 97.5 g of pure 1,1-diphenyl-2-propyn-1-ol (VIII), b.p. 43-44° [10]; yield 93.5%.

Found %: C 86.29; 85.92; H 5.90; 5.78 $C_{15}H_{12}O$. Calculated %: C 86.45; H 5.79

According to Zakharova [4], condensation of benzophenone with acetylene in presence of potassium hydroxide at ordinary pressure gives 1,1-diphenyl-2-propyn-1-ol (VIII) in 30-40% yield, but it is very difficult to isolate it from the mixture with unchanged benzophenone and tetraphenylbutynediol. When 1,1-diphenyl-2-propyn-1-ol (30 g) is exhaustively hydrogenated over a platinum catalyst, it absorbs the theoretical amount of hydrogen (6.6 liters) and gives a quantitative yield of 1,1-diphenyl-1-propanol, m.p. 94-95°.

2-Phenyl-3-buten-2-ol (IX, Ar = C_6H_5)

2-Phenyl-3-butyn-2-ol (I) (128.5 g; m.p. 49°) was hydrogenated in 150 ml of dry methanol in presence of a palladium catalyst [11] supported on calcium carbonate (5% Pd). After the absorption of one molecular proportion of hydrogen (20.8 liters), the hydrogenation was stopped. The selectivity of hydrogenation was verified by testing for an acetylene with ammoniacal silver nitrate (in alcohol), the sensitivity of which is not below 0.5%. When the pure acetylenic alcohol was used, the test did not become negative until exactly one molecular proportion of hydrogen had been absorbed. After the hydrogenation, the catalyst was filtered off, methanol was distilled off, and the residue was vacuum-distilled. The product, amounting to 128 g, was 2-phenyl-3-buten-2-ol (IX, Ar = C_6H_5), b.p. 87-88° (6 mm); n_D^{20} 1.5344 [12].

Found %: C 81.08; 81.28; H 8.14; 8.18 $C_{10}H_{12}O_2$. Calculated %: C 81.10; H 8.11.

When this ethylenic alcohol was exhaustively hydrogenated in presence of a platinum catalyst, it absorbed one molecular proportion of hydrogen and gave 2-phenyl-2-butanol, b.p. 95-96° (13 mm); n_D^{15} 1.5202 [13].

2-p-Methoxyphenyl-3-buten-2-ol (IX, Ar = p-$CH_3OC_6H_4$)

2-p-Methoxyphenyl-3-butyn-2-ol (III) (30 g; m.p. 35°) was hydrogenated as a solution in 50 ml of dry dioxane in presence of a palladium catalyst. When 4025 ml of hydrogen (18°, 755 mm) (i.e., one molecular proportion) had been absorbed, the test for an acetylene became negative and hydrogenation was stopped. The product, amounting to 29 g, was 2-p- methoxyphenyl-3-buten-2-ol (IX, Ar = p-$CH_3OC_6H_4$), b.p. 109-110° (2 mm); n_D^{20} 1.5393; d_4^{20} 1.056; Found MR 52.82; Calculated MR 52.1.

Found % : C 74.16; 74.10; H 7.99; 8.07 $C_{11}H_{14}O_2$. Calculated %: C 74.20; H 7.89.

2-p-Chlorophenyl-3-buten-2-ol (IX, Ar = p-ClC_6H_4)

2-p-Chlorophenyl-3-butyn-2-ol (IV) (52 g; m.p. 43°) was hydrogenated as a solution in 65 ml of dioxane in presence of a palladium catalyst. After the absorption of one molecular proportion of hydrogen (6650 ml at 750 mm and 19°), the test for an acetylene became negative and hydrogenation was stopped. The product was 52 g of 2-p-chlorophenyl-3-buten-2-ol (IX, Ar = p-ClC_6H_4), b.p. 160-107° (5 mm); n_D^{20} 1.5448; d_4^{20} 1.135; Found MR 50.77, Calculated MR 50.71.

Found %: C 65.44; 65.30; H 6.22; 6.19; Cl 20.23; 19.50 $C_{10}H_{11}OCl$. Calculated %: C 65.56; H 6.05; Cl 19.50.

2-Phenyl-1,3-butadiene (X, Ar = C_6H_5)

1. A mixture of 20 g of 2-phenyl-3-buten-2-ol and 0.5 g of finely ground potassium hydrogen sulfate was heated at a bath temperature of 110° in nitrogen at a residual pressure of 10 mm. Crude 2-phenyl-1,3-butadiene (14.8g) came over; drying and redistillation gave 14 g (80%) of pure product, b.p. 62° (13 mm); n_D^{20} 1.5489 [14]. The 2-phenyl-1,3-butadiene so obtained was condensed with maleic anhydride in benzene solution at room temperature for 24 hours, and an almost quantitative yield of the adduct (XI, Ar = C_6H_5), m.p. 104° [14], was obtained. From the residue in the distillation flask, 3.5 g of the dimer of 2-phenyl-1,3-butadiene, b.p. 187-190° (6 mm), was obtained.

2. In nitrogen at a residual pressure of 200 mm, 50 g of 2-phenyl-3-buten-2-ol diluted with an equal amount of water was passed into a catalysis tube filled with granulated alumina (70 g) at a rate of 3 ml per minute. The product was separated from the aqueous layer, dried, and vacuum-distilled. The pure 2-phenyl-1,3-butadiene so obtained amounted to 34.4 g (79%) and had b.p. 62° (13 mm) and n_D^{20} 1.5486; it gave an adduct of m.p. 104° with maleic anhydride. From the residue in the flask, 5.2 g of dimer, b.p. 188-190° (6 mm) was isolated.

2-p-Methoxyphenyl-1,3-butadiene (X, Ar = p-$CH_3OC_6H_4$)

A mixture of 5 g of 2-p-methoxyphenyl-3-buten-2-ol and 5 mg of potassium hydrogen sulfate was heated in nitrogen at a residual pressure of 3 mm at a bath temperature of 100°. The product was dried with calcium chloride and distilled under a reduced pressure of nitrogen. The 2-p-methoxyphenyl-1,3-butadiene obtained (X, Ar = p-$CH_3OC_6H_4$) amounted to 1.5 g (35%) and had b.p. 80° (3 mm); n_D^{20} 1.5554, d_4^{20} 0.934.

Found %: C 82.20; 81.97; H 7.63; 7.69. $C_{11}H_{12}O$. Calculated %: C 82.45; H 7.50.

Condensation of this diene with maleic anhydride in benzene solution gave a quantitative yield of the adduct (XI, Ar = p-$CH_3OC_6H_4$), m.p. 124°.

Found %: C 70.17; 69.93; H 5.69; 5.59. $C_{15}H_{14}O_4$. Calculated %: C 69.99; H 5.45.

The same adduct was obtained in a yield of about 60% also by heating maleic anhydride with 2-p-methoxyphenyl-3-buten-2-ol in boiling xylene for 25 minutes.

When the dehydration of 2-p-methoxyphenyl-3-buten-2-ol was effected with large amounts of potassium hydrogen sulfate (0.5-1%) or in presence of even small amounts of p-toluenesulfonic acid (0.1-0.2%), almost complete polymerization of the resulting 2-p-methoxyphenyl-1,3-butadiene occurred.

2-p-Chlorophenyl-1,3-butadiene (X, Ar = p-ClC_6H_4)

A mixture of 10 g of 2-p-chlorophenyl-3-buten-2-ol and 0.1 g of potassium hydrogen sulfate was heated in nitrogen at a residual pressure of 5 mm at a bath temperature of 100-110°. The distillate was dried with potassium carbonate. Vacuum distillation gave 6.1 g (70%) of 2-p-chlorophenyl-1,3-butadiene, b.p. 64° (3 mm); n_D^{20} 1.5612; d_4^{20} 1.070; Found MR 50.55; Calculated MR 48.91.

Found %: C 72.42; 72.44; H 5.60; 5.52; Cl 22.02; 22.04 $C_{10}H_9Cl$. Calculated %: C 72.80; H 5.47; Cl 21.60.

Condensation of this diene with maleic anhydride in benzene solution gave a quantitative yield of the adduct (XI, Ar = p-ClC_6H_4), m.p. 129°.

Found %: C 64.17; 64.46; H 4.28; 4.37; Cl 14.12; 13.85 $C_{14}H_{11}O_3Cl$. Calculated %: C 64.01; H 4.19; Cl 13.59.

SUMMARY

In presence of potassium hydroxide powder, aliphatic-aromatic and aromatic ketones of the aceto- and benzo-phenone types condense smoothly with acetylene at a pressure of 5-10 atm with formation of the corresponding tertiary acetylenic alcohols in yields of more than 90%. When the 2-aryl-3-butyn-2-ols so obtained are selectively hydrogenated over a palladium catalyst, 2-aryl-3-buten-2-ols are obtained in almost quantitative yield, and dehydration of these gives 2-aryl-1,3-butadienes, which are extremely reactive in polymerization (dimerization) reactions and in the diene condensation.

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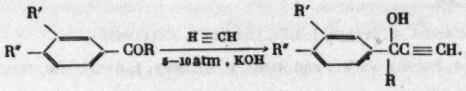
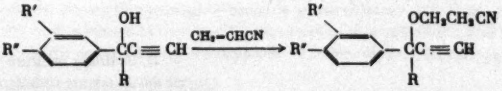
ACETYLENE DERIVATIVES

COMMUNICATION 178. 2-CYANOETHYL ETHERS OF ACETYLENIC ALCOHOLS CONTAINING AROMATIC SUBSTITUENTS

We have recently described [1] the cyanoethylation of 2-phenyl-3-butyn-2-ol and 1,1-diphenyl-2-propyn-1-ol. Extending this investigation, we have studied the cyanoethylation of some other aliphatic-aromatic acetylenic alcohols that are readily prepared by the condensation of acetylene with substituted acetophenones by the method developed in our laboratory [2].

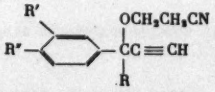


The cyanoethylation of these acetylenic alcohols proceeds smoothly in presence of 40% aqueous potassium hydroxide, the corresponding 2-cyanoethyl ethers being obtained in yields of more than 90%. In this way we prepared the 2-cyanoethyl ethers of the following acetylenic alcohols: 2-p-tolyl-, 2-p-chlorophenyl-, 2-p-bromophenyl-, 2-p-methoxyphenyl-, and 2-(3,4-dichlorophenyl)-3-butyn-2-ols, and 3-phenyl- and 3-p-methoxyphenyl-1-pentyn-3-ols:



Also, we repeated the cyanoethylation of 2-phenyl-3-butyn-2-ol and 1,1-diphenyl-2-propyn-1-ol under somewhat modified conditions, and we obtained better results than those described in the previous paper [1].

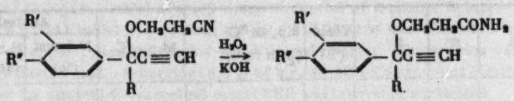
The resulting 2-cyanoethyl ethers of aromatic acetylenic alcohols of general formula



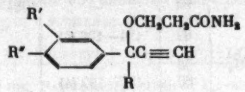
are given in Table 1.

Unlike the 2-cyanoethyl ethers of dialkylethynylmethanols [3], these 2-cyanoethyl ethers of aromatic acetylenic alcohols do not undergo the Mannich reaction, do not give ketones when attempts are made to hydrate the triple bond, and are completely resinified under alcoholysis conditions. By treatment of the 2-

cyanoethyl ethers (I-IX) with alkaline hydrogen peroxide [4] we succeeded in obtaining the corresponding amides in yields of about 90%.



The amides so obtained, general formula



are given in Table 2.

TABLE 1

2-Cyanoethyl ether	R	R′	R″	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	Analysis	
							N found (%)	N calculated (%)
I	CH_3	H	CH_3	97	134—136 (2)	1.5126	6.26 6.01	6.57
II	CH_3	H	Cl	93	140—141 (1)	1.5235	5.90 5.82	6.00
III	CH_3	H	Br	90	153—154 (2)	1.5429	4.66 4.44	4.98
IV	CH_3	H	OCH_3	97	157—160 (3) m.p. 65—66°	—	6.11 6.29	6.11
V	CH_3	Cl	Cl	92	158—159 (1)	1.5404	4.85 5.02	5.22
VI	C_2H_5	H	H	97	127—129 (2)	1.5116	6.13 6.19	6.57
VII	C_2H_5	H	OCH_3	97	159—161 (2)	1.5221	6.01 6.02	5.76
VIII	CH_3	H	H	98	120—123 (4)	1.5131	7.69 7.60	7.04
IX	C_6H_5	H	H	99	m.p. 84—85	—	5.68 5.87	5.36

• From gasoline.

EXPERIMENTAL

Reaction of Acrylonitrile with 2-p-Tolyl-3-butyn-2-ol

A mixture of 58 g (0.36 mole) of 2-p-tolyl-3-butyn-2-ol [b.p. 103-104° (4 mm)] and 8 g of 40% aqueous potassium hydroxide was prepared in a three-necked flask fitted with mechanical stirrer, thermometer, and reflux condenser. The mixture was stirred vigorously for 90 minutes while 21 g (0.4 mole) of acrylonitrile was added. The temperature of the reaction mixture gradually rose to 40-50°. The mixture was stirred for six hours; the temperature fell to 20° during the first two hours and further stirring was continued at room temperature. The mixture was set aside overnight, and on the next day it was neutralized with hydrochloric acid (1 : 1); it was extracted with ether, and the extract was dried with magnesium sulfate. Fractionation gave 75.4 g of the 2-cyanoethyl ether of 2-p-tolyl-3-butyn-2-ol (I), b.p. 134-136° (2 mm) and n_D^{20} 1.5126.

Found %: N 6.26; 6.01 $C_{14}H_{15}NO$. Calculated %: N 6.57.

TABLE 2

Amide	R	R'	R''	Yield (%)	B.p. in °C (p in mm)	M.p., °C	Analysis	
							N found (%)	N calculated (%)
X	CH_3	H	CH_3	76	197—199 (4)	—	6.07 6.18	6.06
XI	CH_3	H	Cl	86	—	73—74*	5.33 5.23	5.58
XII	CH_3	H	Br	88	—	77—78*	4.70 4.71	4.73
XIII	CH_3	H	OCH_3	90	—	—	—	—
XIV	CH_3	Cl	Cl	90	—	106—108**	4.89 4.90	4.89
XV	C_3H_5	H	H	82	194—196 (4)	—	6.02 6.04	6.06
XVI	C_3H_5	H	OCH_3	90	—	—	—	—
XVII	CH_3	H	H	80	189—192 (4)	—	5.84 5.96	6.45
XVIII	C_3H_5	H	H	92	—	117—118***	5.35 5.30	5.02

*From a mixture of diethyl ether and petroleum ether.

**From gasoline.

***From a mixture of benzene and petroleum ether.

Other 2-cyanoethyl ethers listed in Table 1 were prepared similarly.

Reaction of Acrylonitrile with 3-Phenyl-1-pentyn-3-ol

Acrylonitrile (12 g, i.e., 0.26 mole) was added over a period of one hour to a vigorously stirred mixture of 32 g (0.2 mole) of 3-phenyl-1-pentyn-3-ol (b.p. 86-87° (2 mm)), 10 ml of dioxane, and 3 g of 40% aqueous potassium hydroxide. The temperature of the mixture rose spontaneously to 30° and then fell to room temperature in the course of six hours. On the next day the reaction mixture was neutralized with hydrochloric acid (1:1) and was stirred with 5 g of ferrous sulfate for 30 minutes (to destroy oxides). The mixture was extracted with ether, and the extract was dried with magnesium sulfate. Vacuum fractionation gave 40.8 g of the 2-cyanoethyl ether of 3-phenyl-1-pentyn-3-ol (VI), b.p. 127-129° (2 mm) and n_D^{20} 1.5116.

Found %: N 6.13; 6.19 $C_{14}H_{15}NO$. Calulated %: N 6.57.

The 2-cyanoethyl ether (VII) was synthesized in the same way, but without the use of dioxane.

Reaction of Acrylonitrile with 2-Phenyl-3-butyn-2-ol

Acrylonitrile (28 g, i.e., 0.53 mole) was added over a period of 90 minutes to a vigorously stirred mixture of 73 g (0.5 mole) of 2-phenyl-3-butyn-2-ol [b.p. 106-107° (15 mm)], 25 ml of dioxane, and 10 g of 40% aqueous potassium hydroxide. At first the temperature of the mixture rose spontaneously to 40°, and it then fell to room temperature in the course of two hours. On the next day the mixture was neutralized with hydrochloric acid (1:1) and treated as in the preceding experiment (preparation of the 2-cyanoethyl ether (VI)). The product, amounting to 91.4 g, was the 2-cyanoethyl ether of 2-phenyl-3-butyn-2-ol (VIII), b.p. 120-123° (4mm); and n_D^{20} 1.5127, and 5.8 g of the acetylenic alcohol was recovered unchanged.

Reaction of Acrylonitrile with 1,1-Diphenyl-2-propyn-1-ol

A mixture of 35 g (0.17 mole) of 1,1-diphenyl-2-propyn-1-ol [b.p. 125-126° (1 mm)], 10 g (0.19 mole) of acrylonitrile, 35 ml of dioxane, and 5 g of 40% aqueous potassium hydroxide was stirred for six hours and then set aside overnight. The usual treatment gave 43.2 g of the 2-cyanoethyl ether of 1,1-diphenyl-2-propyn-1-ol (IX), b.p. 188-196° (6 mm), m.p. 84-85° (from petroleum ether).

Reaction of the 2-Cyanoethyl Ether of 2-Phenyl-3-butyn-2-ol (VIII) with Diethylamine and Paraform

1. A mixture of 19.9 g (0.1 mole) of the 2-cyanoethyl ether of 2-phenyl-3-butyn-2-ol, 8.0 g (0.11 mole) of diethylamine, 3.3 g (0.11 mole) of paraform, and 12 ml of dioxane was refluxed for 14 hours. Dioxane was distilled off at the water pump, and the residue was dissolved in ether. The solution was dried with magnesium sulfate and vacuum-fractionated. A fraction (6.8 g) of b.p. 85-88° (2.5 mm) was obtained and was not studied further, and 8.2 g of the original 2-cyanoethyl ether (VIII) was recovered unchanged.

2. A mixture of 10 g (0.05 mole) of the 2-cyanoethyl ether (VIII), 6 g (0.55 mole) of diethylamine hydrochloride, 1.8 g (0.06 mole) of paraform, 10 ml of dioxane, and 5 ml of isopropyl alcohol was boiled for 20 hours. Alcohol and dioxane were distilled off at the water pump, and the residue was treated with ether. From the ethereal solution 7.5 g of the 2-cyanoethyl ether (VIII) was recovered unchanged. The ether-insoluble residue was saturated with potassium carbonate and extracted with ether. The ether extract was dried with magnesium sulfate and distilled: 0.4 g of a substance of b.p. 132-138° (3 mm) was obtained.

Reaction of the 2-Cyanoethyl Ether of 1,1-Diphenyl-2-propyn-1-ol (IX) with Diethylamine and Paraform

A mixture of 26.1 g (0.1 mole) of the 2-cyanoethyl ether of 1,1-diphenyl-2-propyn-1-ol, 8 g (0.11 mole) of diethylamine, 3.3 g (0.11 mole) of paraform, and 30 ml of dioxane was refluxed for 14 hours. Dioxane was distilled off under somewhat reduced pressure, and the residue was dissolved in 50 ml of ether and treated with hydrochloric acid (1 : 1). From the ethereal solution 19.3 g of the 2-cyanoethyl ether (IX) was recovered. The acid extract was saturated with potassium carbonate and extracted with ether. Only resinous products were obtained from the extract.

Attempts to Hydrate the 2-Cyanoethyl Ether (VIII)

A mixture of 20 g (0.1 mole) of the 2-cyanoethyl ether (VIII), 2 g of mercuric sulfate, 25 ml of water, 50 ml of dioxane, and 5 drops of concentrated sulfuric acid was prepared in a three-necked flask fitted with mechanical stirrer, thermometer, and reflux condenser. The mixture was stirred at 90° for three hours and then left overnight. The reaction mixture was saturated with potassium carbonate and extracted with ether. The extract was dried with magnesium sulfate and vacuum-fractionated. A light-yellow oil [18 g; b.p. 95-115° (5 mm)] was obtained and was not investigated further.

Alcoholysis of the 2-Cyanoethyl Ether (VIII)

A mixture of 10 g (0.05 mole) of the 2-cyanoethyl ether (VIII) and 75 ml of methanol containing 15 g of dry hydrogen chloride was left in a round-bottomed flask for about four hours at room temperature. The flask was provided with a still head, and methanol was removed at 20° at the water pump. Water (100 ml) was added to the residue, and the mixture was stirred and saturated with potassium carbonate; it was then extracted with ether. A dark-colored sticky resin remained after removal of ether.

Partial Hydrolysis of the 2-Cyanoethyl Ether of 3-Phenyl-1-pentyn-3-ol (VI) with Alkaline Hydrogen Peroxide

A mixture of 11 g (0.051 mole) of the 2-cyanoethyl ether of 3-phenyl-1-pentyn-3-ol, 240 ml of 4% hydrogen peroxide, 2.5 ml of 40% aqueous potassium hydroxide, and 150 ml of acetone was prepared in a three-necked flask fitted with mechanical stirrer, thermometer, and reflux condenser. The mixture was stirred, and the temperature rose spontaneously to 30-35°, when the evolution of bubbles of oxygen began. The reaction mixture was stirred at 50° for five hours, and toward the end of this period the brisk evolution of oxygen had almost completely stopped. The contents of the three-necked flask were transferred to a Favorsky flask, and acetone was distilled off at 50-60° under reduced pressure. The aqueous layer was saturated with potassium carbonate and extracted with ethyl acetate. The extract was dried with magnesium sulfate and vacuum-fractionated. The product, amounting to 9.9 g, was the amide (XV), b.p. 194-196° (4 mm).

Found %: N 6.02; 6.04 $C_{14}H_{17}NO_2$. Calculated %: N 6.06.

The other amides listed in Table 2 were prepared similarly. The amides (XI), (XII), (XIV), and (XVIII) were not distilled, but were purified by crystallization. The amides (XIII) and (XVI) were not purified since they formed very viscous undistillable oils.

Partial Hydrolysis of the 2-Cyanoethyl Ether of 1,1-Diphenyl-2-propyn-1-ol (IX) with Alkaline Hydrogen Peroxide

A mixture of 13 g (0.05 mole) of the 2-cyanoethyl ether of 1,1-diphenyl-2-propyn-1-ol (IX), 250 ml of 4% hydrogen peroxide, 2.5 g of 40% potassium hydroxide solution, and 300 ml of acetone was stirred for six hours at 50°. Acetone was distilled off, and the aqueous residue was saturated with potassium carbonate and extracted with ethyl acetate. After removal of ethyl acetate, 12.9 g of the amide (XVIII), m.p. 117-118° (from a mixture of benzene and petroleum ether) was obtained.

Found %: N 5.35; 5.30 $C_{17}H_{17}NO_2$. Calculated %: N 5.02.

The amides (XI), (XII), and (XVIII) remain after the removal of ethyl acetate in the form of thick oils that are very difficult to crystallize. To accelerate crystallization, these amides were dissolved in alcohol and precipitated out with water; they then crystallized in the course of a night. The amide (XIV) was obtained in the crystalline state immediately after removal of acetone.

SUMMARY

1. Some tertiary acetylenic alcohols containing aromatic radicals were cyanoethylated. The new 2-cyanoethyl ether of aromatic acetylenic alcohols were obtained in yields of greater than 90%.

2. These 2-cyanoethyl ethers of aromatic acetylenic alcohols do not readily undergo the Mannich reaction and the reaction of hydration of the triple bond. They are completely resinified when attempts are made to alcoholyze the nitrile group.

3. These 2-cyanoethyl ethers are converted into the corresponding amides in good yield by the action of alkaline hydrogen peroxide.

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* Original Russian Pagination. See C. B. Translation.

** In Russian.

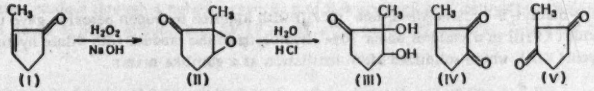
α-KETO EPOXIDES AND THEIR REACTIONS

COMMUNICATION 6. α-KETO EPOXIDES FROM CYCLIC KETONES

I. N. Nazarov and A. A. Arkhem

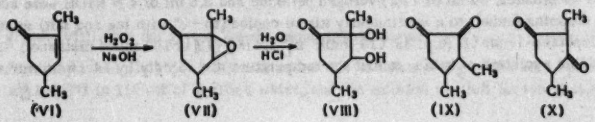
In previous communications [1] we described the preparation of aliphatic α-keto epoxides and keto diepoxides by the oxidation of the corresponding α,β-unsaturated ketones with alkaline hydrogen peroxide. It was considered to be of interest to apply this reaction also for the oxidation of α,β-unsaturated cyclic ketones with the object of obtaining cyclic α-keto epoxides, because only isolated members of this class of compounds—mainly α-keto epoxides from unsaturated cyclic ketones of the terpene series [2-4]—have been prepared. It should be noted that, until recently, the view was prevalent in the literature that α,β-unsaturated cyclic ketones are difficult to oxidize with alkaline hydrogen peroxide [5] and that the cyclic α-keto epoxides that are formed in small amount in this reaction are unstable compounds, which readily lose their epoxide oxygen during distillation [2]. Interest in cyclic epoxides has grown appreciably recently in connection with work on the partial synthesis of corticosteroids, in particular, cortisone [6], which are known to have a hydroxy or carbonyl group at C-11 and also a hydroxy group at C-17.

We began by studying the oxidation of the simplest cyclic α,β-unsaturated ketones with the intention of proceeding further to the oxidation of more complex polycyclic systems, including tetracyclic ketones related to steroids. Oxidation of 2-methyl-2-cyclopenten-1-one (I) with alkaline hydrogen peroxide in methanol gave 2,3-epoxy-2-methylcyclopentanone (II) in a yield of about 40%; hydrolysis of this product with hot 3% hydrochloric acid gave a low yield of a crystalline substance of m.p. 104-105°, which corresponded in analysis to a diketone of formula (IV) or (V):



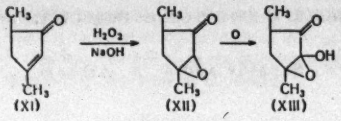
The product is acid to Congo red, and with aqueous ferric chloride it gives a violet coloration that changes to red on addition of sodium acetate. The hydrolysis of the α-keto epoxide (II) is probably accompanied by rearrangement of the resulting keto glycol (III) with migration of the methyl group and formation of the α-diketone (IV) instead of the expected β-diketone (V). According to the literature [7], the α-diketone (IV) melts at 105-106°, whereas the β-diketone (V) melts at 212° [8]. We did not succeed in isolating the corresponding keto glycol (III) in the pure state.

By the action of alkaline hydrogen peroxide on 2,4-dimethyl-2-cyclopenten-1-one (VI) [9] in methanol solution, 2,3-epoxy-2,4-dimethylcyclopentanone (VII) was obtained in a yield of about 30%.



Hydrolysis of the keto epoxide (VII) with dilute hydrochloric acid gave a product of m.p. 84-87° corresponding in analysis to the diketone (IX) or (X). In this case, together with the diketone, we obtained also the keto glycol (VIII). When the hydrolysis of the keto epoxide (VII) was effected with water, the main reaction product was the keto glycol (VIII), which probably consisted of a mixture of geometric isomers.

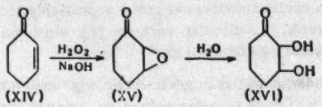
The oxidation of 3,5-dimethyl-2-cyclopenten-1-one (XI) [10] was more difficult, and we did not succeed in isolating the α-keto epoxide (XII) in the pure state: it was characterized only in the form of its semicarbazone. In the oxidation of the ketone (XI), the formation of the keto epoxide (XII) was accompanied by the formation of a small amount of the hydroxy keto epoxide (XIII), m.p. 68°, corresponding to the further oxidation of the keto epoxide (XII):



(XI) (XII) (XIII)

We met a similar oxidation previously in the case of mesityl oxide [11].

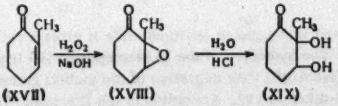
Oxidation of 2-cyclohexen-1-one (XIV) with alkaline hydrogen peroxide gave a 50% yield of the corresponding α-keto epoxide (XV), which was hydrolyzed by water in the cold with formation of the crystalline α-keto glycol (XVI), probably in the transconfiguration.



(XIV) (XV) (XVI)

In the hydrolysis of the keto epoxide (XV), a crystal hydrate of (XVI), m.p. 115°, was first formed. This hydrate contained one molecule of water to every six of the glycol, and this water was lost when the hydrate was sublimed with formation of the anhydrous keto glycol (XVI), m.p. 87°. According to the results of Kötz and Richter [12], 2-cyclohexen-1-one (XIV) cannot be oxidized with hydrogen peroxide.

Oxidation of 2-methyl-2-cyclohexen-1-one (XVII) with alkaline hydrogen peroxide gave the corresponding α-keto epoxide (XVIII) in a yield of about 70%. Hydrolysis of the product with dilute hydrochloric acid gave the keto glycol (XIX), which solidified after distillation as a gumlike mass:



(XVII) (XVIII) (XIX)

EXPERIMENTAL

Preparation of the α-Keto Epoxide (II)

In the course of 45 minutes, 50 ml of 12% hydrogen peroxide and 3.5 ml of 4 N NaOH were added simultaneously from two dropping funnels to a continuously stirred cooled (to −8° with ice and salt) solution of 15 g of 2-methyl-2-cyclopenten-1-one (I) [b.p. 49° (13 mm); n_D^{22} 1.4780] [13] in 100 ml of methanol. Reaction proceeded with appreciable evolution of heat: at first the temperature rose rapidly by 14° (from −8° to +6°), but

was then maintained in the range from −5° to −2°. Forty minutes after the addition of the oxidizing agent, only 0.4 g of hydrogen peroxide was present in the reaction mixture. The colorless solution was neutralized with dilute sulfuric acid (8 ml of 10% sulfuric acid), excess of hydrogen peroxide was decomposed with manganese dioxide, precipitated sodium sulfate was filtered off, and the solution was diluted with an equal amount of water, saturated with ammonium sulfate, and extracted with ether. The ether extracts were dried with anhydrous sodium sulfate, ether was distilled off, and the residue was vacuum-fractionated. The product, amounting to 8 g, was 2,3-epoxy-2-methylcyclopentanone (II) in the form of a colorless liquid, b.p. 56.5-57° (10 mm); n_D^{20} 1.4537; d_4^{20} 1.0902; Found MR 27.80; Calculated MR 27.86.

Found %: C 64.20; 64.47; H 7.36; 7.20 $C_6H_8O_2$. Calculated %: C 64.29; H 7.14.

Hydrolysis of the Keto Epoxide (II) with Dilute Hydrochloric Acid

Concentrated hydrochloric acid (5 ml) was added to a solution of 5 g of the epoxide (II) (b.p. 50-55° (11 mm); n_D^{20} 1.4630) in 50 ml of distilled water (the epoxide dissolves completely in 6 volumes of water). The solution was left overnight at room temperature and was then boiled for 30 minutes. The hydrochloric acid present was neutralized with sodium bicarbonate, the solution was repeatedly extracted with ether, and the ether extracts were dried with anhydrous sodium sulfate. After removal of ether, the sirupy residue (about 2.5 g) was cooled with ice and salt, and 0.5 g of crystals and about 2 g of a thick oil were obtained. When the liquid product was distilled, about 0.5 g of a substance of b.p. 65-70° (11 mm) and n_D^{20} 1.4797 came over; it was not investigated further. The residue, which turned into a thick paste, was combined with the above-mentioned crystals and recrystallized from alcohol; a small quantity of white mat needles, m.p. 104-105°, was obtained.

Found %: C 64.50; 64.60; H 7.27; 7.43 $C_6H_8O_2$. Calculated %: C 64.29; H 7.14.

According to the literature [7], the α-diketone (IV) melts at 105-106°, whereas the isomeric β-diketone (V) melts at 212° [8].

Preparation of the α-Keto Epoxide (VII)

Under the conditions described above, 100 g of 2,4-dimethyl-2-cyclopenten-1-one (VI) (b.p. 167-169°; n^{20} 1.4681) [9] in 200 ml of methanol was oxidized with the aid of 120 ml of 28% hydrogen peroxide and 20 ml of 4 N NaOH. By cooling and regulation of the rate of adding oxidizing agent, the reaction temperature was maintained at 8-10°. The oxidizing agent was added over a period of one hour. Reaction proceeded with evolution of heat and lasted until the theoretical amount of oxygen had been consumed (2.5 hours). Fractionation of the reaction product through a column gave 20 g of 2,3-epoxy-2,4-dimethylcyclopentanone (VII) as a colorless mobile liquid of pungent odor, b.p. 51° (5 mm); n_D^{20} 1.4445; d_4^{20} 1.0211; Found MR 32.81; Calculated MR 32.48.

Found %: C 66.52; 66.45; H 8.73; 8.53 $C_7H_{10}O_2$. Calculated %: C 66.66; H 7.94.

Found: M 127, 123 (in benzene) $C_7H_{10}O_2$. Calculated: M 126.

Hydrolysis of the α-Keto Epoxide (VII)

a) A mixture of 18 g of the keto epoxide (VII) (b.p. 73.5° (23 mm); n_D^{20} 1.4452) and 140 ml of distilled water was heated in a sealed tube at 155-160° for ten hours. Removal of water under reduced pressure gave about 10 g of a thick yellow sirup. Two vacuum fractionations of this gave 3 g of the keto glycol (VIII) as a thick faintly colored sirup, b.p. 124-124.5° (3 mm); n_D^{20} 1.4848; d_4^{20} 1.1546; Found MR 35.73; Calculated MR 35.39.

Found %: C 58.85; 58.81; H 8.48; 8.64 $C_7H_{12}O_3$. Calculated %: C 58.38; H 8.34.

The keto glycol (VIII) does not give a 2,4-dinitrophenylhydrazone.

b) Concentrated hydrochloric acid (7 ml) was added to a solution of 6 g of the keto epoxide (VII) (b.p. 69.5-71° (19 mm); n_D^{18} 1.4477) in 110 ml of distilled water, and the solution was left for ten days at room temperature.

The solution was then heated in a boiling water bath for two hours. The solution, which had turned yellow, was evaporated to half bulk in a vacuum, neutralized with potassium carbonate, and extracted with ether. The extract was dried with anhydrous magnesium sulfate, and ether was distilled off. Vacuum fractionation of the residue gave 0.5 g of a substance of b.p. 66° (1 mm) and n_D^{19} 1.4930, which rapidly solidified to colorless crystals. These crystals became pink after two hours, and after two days they turned into a liquid, which could not then be crystallized. Also, it was not found possible to recrystallize the crystals. The crystals of the freshly distilled product, probably the diketone (IX), were washed on the filter with petroleum ether and were then found to melt at 84-87°.

Found %: C 65.99; 65.22; H 8.04; 8.02 $C_7H_{10}O_2$. Calculated %: C 66.66; H 7.94.

When the substance was not analyzed immediately after isolation, a very low carbon content was obtained. The substance did not form a dioxime. It gave a blue coloration with aqueous ferric chloride.

Preparation of the α-Keto Epoxide (XII)

3,5-Dimethyl-2-cyclopenten-1-one (XI) (50 g; b.p. 180-182°; n_D^{20} 1.4785) [10] was oxidized with alkaline hydrogen peroxide as described above. Fractional distillation of the reaction products gave 15 g of 2,3-epoxy-3,5-dimethylcyclopentanone (XII) as a colorless liquid, b.p. 59.5-60° (8 mm); n_D^{20} 1.4568; d_4^{20} 0.9951. Elementary analysis indicated that the substance contained some of the original ketone as impurity. The ketone epoxide (XII) gave a semicarbazone of m.p. 173-174° with decomposition. A mixture of this with the semicarbazone of the original ketone (XI) (m.p. 175-176°) melted at 165-173°.

Found %: N 23.12; 23.83 $C_8H_{13}O_2N_3$. Calculated %: N 22.95.

In addition, about 4 g of the hydroxy keto epoxide (XII) was obtained in the form of colorless needles, m.p. 68° (from a mixture of diethyl ether and petroleum ether), b.p. 110-112° (7 mm), and n_D^{17} 1.4662.

Found %: C 59.22; 59.23; H 7.31; 7.17 $C_7H_{10}O_3$. Calculated %: C 59.15; H 7.04.

Found: M 141; 131 (in benzene) $C_7H_{10}O_3$. Calculated: M 142.

This substance did not give a semicarbazone.

Analysis by the Chugaev-Tserevitinov method gave only about 6% of hydroxyl groups, instead of the 12% required theoretically.

Preparation of the α-Keto Epoxide (XV)

Over a period of 40 minutes, 24 ml of 15% hydrogen peroxide solution (1 mole) and 5 ml of 4 N NaOH were added dropwise simultaneously to a vigorously stirred, cooled (ice and salt) solution of 15 g of 2-cyclohexen-1-one (XIV) (b.p. 70° (21 mm), n^{21} 1.4840) [13] in 80 ml of methanol. Much heat was evolved at first, but the temperature of the reaction mixture was maintained at not above 0°. Two hours after the additions of the oxidizing agent, 1.5 g of hydrogen peroxide remained in the solution. After a further one hour alkali was neutralized with dilute sulfuric acid and residual hydrogen peroxide was decomposed with manganese dioxide. The solution was filtered, methanol was distilled off under reduced pressure, and the product was extracted with ether. The extract was dried with anhydrous magnesium sulfate and vacuum-distilled. The product, amounting to 8 g, was 2,3-epoxycyclohexanone (XV), a colorless liquid, volatile in steam and methanol vapor, b.p. 43.5° (1 mm); n_D^{20} 1.4720; d_4^{20} 1.1313; Found MR 27.72; Calculated MR 27.86.

Found %: C 63.63; 63.74; H 7.62; 7.75 $C_6H_8O_2$. Calculated %: C 64.29; H 7.14.

When kept for a long time, the keto epoxide (XV) turned yellow with gradual increase in refractive index (in 18 months n_D^{20} rose to 1.4810).

Found: M 106; 116 (in benzene) $C_6H_8O_2$. Calculated: M 112.

The semicarbazone of the keto epoxide (XV) was precipitated immediately, but we could not recrystallize it because, after being dissolved, it did not come out of solution in a crystalline form. Washing on the filter with methanol and ether gave colorless crystals, m.p. 183-185° with decomposition (the semicarbazone of the original cyclohexenone melted at 161°).

Found %: N 24.62; 24.79 $C_7H_{11}O_2N_3$. Calculated %: N 24.85.

Hydrolysis of the α-Keto Epoxide (XV)

The keto epoxide (XV) (2.5 g) was dissolved in 30 ml of distilled water, and the solution was set aside for 15 days at room temperature. Water was distilled off under reduced pressure, and the sirupy residue (about 2.7 g) solidified with evolution of heat when seeded with a small crystal (taken off a capillary). The resulting finely crystalline powder was insoluble in the usual organic solvents and sparingly soluble in hot water. Repeated washing on the filter with alcohol and ether and drying in a vacuum desiccator over phosphoric oxide gave a product of m.p. 115° (the cooled melt remelts at 82-83°).

Found %: C 54.73; 54.46; H 7.80; 7.70 $(C_6H_{10}O_3)_6 + H_2O$. Calculated %: C 54.13; H 7.77.

Found %: OH 29.20 (in pyridine) $[C_6H_8O(OH)_2]_6 + H_2O$. Calculated %: OH 29.95.

When the crystals were sublimed at 1.5 mm and at 96-97°, they lost their water of crystallization and were converted into the anhydrous keto glycol (XVI), which formed colorless crystals, m.p. 87° (from a mixture of diethyl ether and petroleum ether), readily soluble in the usual organic solvents.

Found %: C 55.29; 55.34; H 7.74; 7.61 $C_6H_{10}O_3$. Calculated %: C 55.31; H 7.61.

Found: M 132 (in benzene) $C_6H_{10}O_3$. Calculated: M 130

Found %: OH 31.57 (in pyridine) $C_6H_8O(OH)_2$. Calculated %: OH 26.15.

Preparation of the α-Keto Epoxide (XVIII)

2-Methyl-2-cyclohexen-1-one (XVII) (30 g; b.p. 62° (13.5 mm); n_D^{20} 1.4828) [13] was oxidized in 100 ml of methanol with the aid of 64 ml of 19% hydrogen peroxide and 10 ml of 4 N NaOH, as described above. The oxidation reaction was complete in about two hours. Vacuum fractionation gave 27 g (80%) of the α-keto epoxide (XVIII) in the form of a colorless liquid having a feeble characteristic odor, b.p. 80.5-81° (16 mm); n_D^{20} 1.4629; d_4^{20} 1.0753; Found MR 32.27; Calculated MR 32.48.

Found %: C 67.02; 66.93; H 8.18; 8.26 $C_7H_{10}O_2$. Calculated %: C 66.67; H 7.94.

Found: M 116 (in benzene) $C_7H_{10}O_2$. Calculated: M 126.

The semicarbazone of the keto epoxide (XVIII) was precipitated immediately in the form of colorless well-formed crystals, m.p. 120-124° with decomposition, but we did not succeed in recrystallizing it; we therefore washed with ether on the filter and dried it in a vacuum desiccator over phosphoric anhydride.

Found %: N 22.60; 23.00 $C_8H_{13}O_2N_3$. Calculated %: N 22.95.

Hydrolysis of the Keto Epoxide (XVIII)

Water (80 ml) was added to 4 g of the keto epoxide (XVIII), and the mixture was set aside overnight at room temperature. On the next day, 7 ml of concentrated hydrochloric acid was added to the reaction mixture, which was then heated at 90° for 15 minutes. The solution was cooled, saturated with potassium carbonate, and extracted with ether. The extract was dried with magnesium sulfate. Vacuum fractionation gave 1.5 g of the glycol (XIX) as a colorless viscous sirup, b.p. 102° (2.5 mm) and n_D^{17} 1.4920; it was solidifying even during the distillation into a vitreous mass. Before being analyzed, the glycol (XIX) was kept for three days in a vacuum desiccator over phosphoric oxide.

Found %: C 58.13; 58.46; H 8.40; 8.51 $C_7H_{12}O_3$. Calculated %: C 58.33; H 8.33.

Found: M 149; 143 (in benzene) $C_7H_{12}O_3$. Calculated: M 144

Found %: OH 25.11; 26.48 (in pyridine) $C_7H_{12}O_3$. Calculated %: OH 23.61.

SUMMARY

1. A study was made of the oxidation of the simplest alicyclic α,β-unsaturated ketones with alkaline peroxide. The corresponding cyclic α-ketone epoxides were obtained in 30-80% yield.

2. It was shown that, contrary to indications in the literature, epoxides derived from alicyclic α,β-unsaturated ketones are relatively stable compounds which can be vacuum-distilled without decomposition.

3. A study was made of the hydrolysis of cyclic α-keto epoxides to the corresponding α-keto glycols. In some cases it is accompanied by rearrangement with formation of cyclic diketones.

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DEMETHYLATION AND ISOMERIZATION OF o-XYLENE OVER ALUMINOSILICATES

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Linear aromatic polyesters are widely used for the manufacture of synthetic fibers. For example, polyethylene terephthalate (Terylene), the synthesis of which is based on terephthalic acid and ethylene glycol, has recently become widely acclaimed for its valuable properties and there has been a corresponding great increase in the scale of its manufacture. In this connection the development of a rational method of synthesizing p-xylene becomes of great practical importance. One promising direction in which the solution of the problem of the manufacture of p-xylene may be sought is its preparation on the basis of the isomerization of m- and o-xylenes.

Several investigations have been devoted to the isomerization of xylenes. Dobryansky and Saprykin [1] subjected o-, m-, and p-xylenes to pyrolysis and investigated the reaction products. In the transformation of o-xylene in a porcelain tube at 750° they observed the formation of 12.8% of toluene, 20.5% of high-boiling aromatic hydrocarbons, and 14.8% of gas. It was shown that the xylene fraction of the pyrolyzate contained some m- and p-xylenes as well as o-xylene. With rise in temperature from 700° to 770°, the m-xylene content increased from 5.0% to 38.2%. The formation of p-xylene was of minor significance, and only at 770° did its content attain 10.6%.

In the pyrolysis of p-xylene, the yields of toluene, higher aromatic hydrocarbons, gaseous products, and unchanged xylene were 13.3, 49.2, 19.3, and 14.8%, respectively, on the original material. An appreciable amount of o- and m-isomers was formed. In the products of the thermal decomposition of m-xylene at temperatures below 700° no o- and p-xylenes were detected. Baddeley and Kenner [2], in a study of the pyrolysis products of m-xylene obtained by passing the vapor through a quartz tube at 800°, found not only benzene, toluene, naphthalene, anthracene, and compounds of still higher boiling point, but also small amounts of o- and p-xylenes. It was thus shown that in the pyrolysis of xylenes, apart from the main decomposition and condensation reactions, partial thermal isomerization occurs. m-Xylene has comparatively high thermal stability to isomerization.

Investigations have been carried out also on the catalytic isomerization of various alkyl benzenes. Thus, Anschutz and Immendorf [3] and Heise and Töll [4] studied the isomerization of xylenes in presence of aluminum chloride. There are references to the isomerization of pseudocumene into mesitylene [5], of durene and isodurene into prehnitene [6], etc. A review of the literature on the isomerization of hydrocarbons, including aromatic hydrocarbons, is given in the monograph of Egloff, Hulla, and Komarewsky [7].

Norris and coworkers [8, 9] studied the isomerization of xylenes in presence of aluminum chloride, reaction being promoted by a stream of hydrogen chloride. It was shown that the extent to which isomerization of xylenes occurred depended to a considerable extent on the reaction temperature and consumption of aluminum chloride. For a contact time of 25 minutes at 94°, o-xylene is isomerized with formation of 38.6% of m-xylene and 13.4% of p-xylene. Aluminum chloride has a somewhat lower isomerizing effect of m-xylene. For a contact time of 20 hours at 50°, the isomerization product from m-xylene was found to contain 15.0% of o-xylene and 16.0% of p-xylene.

TABLE 1

Dealkylation of o-Xylene with Associated Alkylation of Benzene

Characteristics of experiment	Original mixture: molar ratio of benzene to o-xylene = 2:1		Temperature 525°, rate 0.5:1, duration of cycle 50 minutes							
			Experiment No. 1641		Experiment No. 1629		Experiment No. 1630		Experiment No. 1631	
			Pressure 6 atm		Pressure 15 atm		Pressure 15 atm		Pressure 15 atm	
	Yield of fraction (% by wt.)	n_D^{20}	Yield of fraction (% by wt.)	n_D^{20}	Yield of fraction (% by wt.)	n_D^{20}	Yield of fraction (% by wt.)	n_D^{20}	Yield of fraction (% by wt.)	n_D^{20}
1	2		3		4		5		6	
Material balance sheet (% by wt.)										
Catalyzate	—		97.1		94.3		95.17		94.73	
Gas	—		0.78		2.31		1.71		2.2	
Coke	—		0.87		2.2		1.96		1.95	
Losses	—		1.26		1.19		1.16		1.1	
Characteristics of catalyzate										
Start of boiling (°C)	79		79.5		80		80		80	
From 80 to 83	58	1.5011	49.40	1.5010	48.37	1.5009	47.90	1.5012	49.37	1.5012
From 83 to 88	—	—	0.50	1.4995	0.53	1.5000	0.73	1.5011	0.33	1.5008
From 88 to 95	0.43	—	0.55	1.4973	0.75	1.4995	0.48	1.5008	0.50	1.5002
From 95 to 103	0.30	—	0.65	1.4980	0.92	1.4984	0.60	1.5000	0.37	1.4995
From 103 to 108	—	—	0.47	1.4972	0.85	1.4982	0.67	1.4991	0.73	1.4985
From 108 to 113	—	—	20.14	1.4966	27.07	1.4969	28.13	1.4972	27.07	1.4972
From 113 to 118	0.35	—	0.65	1.4961	0.90	1.4962	0.60	1.4972	0.62	1.4970
From 118 to 125	—	—	0.60	1.4961	0.77	1.4965	0.78	1.4970	0.60	1.4970
From 125 to 132	0.47	—	0.57	1.4954	0.80	1.4965	0.77	1.4969	0.83	1.4972
From 132 to 136	—	—	0.68	1.4958	0.70	1.4969	0.73	1.4970	0.85	1.4971
From 136 to 142	1.40	1.5025	17.75	1.4972	11.50	1.4972	11.62	1.4982	11.65	1.4979
From 142 to 143	1.48	1.5042	0.68	1.4982	0.75	1.5008	0.70	1.5005	0.65	—
From 143 to 146	34.93	1.5050	1.76	1.5001	1.70	1.5006	0.98	1.5010	0.90	1.5010
From 146 to 150	—	—	0.72	1.5004	1.00	1.5014	0.9	1.5012	0.80	1.5012
From 150 to b.p.	—	—	2.12	1.5005	1.88	1.5020	1.75	1.5013	2.13	1.5019

TABLE 1 (cont'd)

1	2	3	4	5	6
End of boiling (°C)	145	162.5	164	162	162.8
Total yield	97.36	96.27	97.50	97.36	97.40
Residue	1.87	2.80	2.25	1.87	1.90
Losses	0.77	0.93	0.25	0.77	0.70
d_4^{20}	0.8796	0.8724	0.8732	0.8725	0.8722
n_D^{20}	1.5012	1.4995	1.5000	1.5000	1.4992
Iodine value	0.0	0.0	0.0	0.0	0.0
Sulfonatables (%)	100%	100%	100%	100%	100%
Characteristics of Fractions 78-83° fraction					
Yield (% by weight of catalyzate)	58.0	49.40	48.37	47.90	49.37
d_4^{20}	0.8788	0.8788	0.8778	0.8780	0.8778
n_D^{20}	1.5011	1.5010	1.5009	1.5012	1.5012
Bromine value	0.02	0.04	0.06	0.04	0.05
Sulfonatables (%)	100	100	100	100	100
108-113° fraction					
Yield (% by weight of catalyzate)	0.35	20.15	27.07	28.13	27.07
d_4^{20}	—	0.8669	0.8669	0.8662	0.8674
n_D^{20}	—	1.4966	1.4969	1.4972	1.4972
Bromine value	—	0.04	0.03	0.03	100%
Sulfonatables (%)	—	—	—	—	—
136-142° fraction					
Yield (% by weight of catalyzate)	34.93*	17.75	11.50	11.62	11.65
d_4^{20}	0.8800	0.8647	0.8648	0.8647	0.8650
n_D^{20}	1.5050	1.4972	1.4972	1.4982	1.4979
Bromine value	0.03	0.06	0.04	0.04	0.05
Sulfonatables (%)	100	100	100	100	100

In one of our previous papers [10] we gave the results of a study of the isomerization of m- and o-xylenes over aluminosilicates. At not above 450° and for a rate of 0.5 : 1 [ratio of volume of reactant passing per hour to volume of catalyst], isomerization proceeded to a maximum extent in experiments at atmospheric pressure and in those carried out under vacuum conditions. It was shown that increase in pressure favors the reaction of disproportionation with formation of appreciable amounts of toluene and trimethylbenzenes.

Bodeker and Erner [11] studied the vapor-phase catalytic isomerization of commercial m-xylene (84% m-xylene, 9% p-xylene, 5% o-xylene, and about 2% ethylbenzene) over aluminosilicate cracking catalysts. At 515° and for a rate of feed of 0.7 at atmospheric pressure, in addition to the isomerization of xylene, the reaction of redistribution of methyl groups occurred. The catalyzate consisted of a mixture of 1.2% of benzene, 13% of toluene, 32.2% of m-xylene, 18.9% of p-xylene, 13.0% of o-xylene, 5.10% of ethylbenzene, and 16.5% of C_9 aromatic hydrocarbons. Some experiments were carried out under vacuum conditions. The p- and o-xylene contents were then increased from 9 and 5% in the raw material to 18-20 and 7-9% in the catalyzate. The use of a vacuum, however, favored the formation of an appreciable amount of ethylbenzene.

EXPERIMENTAL

Experiments were carried out on the demethylation and isomerization of o-, m-, and p-xylenes. The present paper gives the results on the isomerization of o-xylene and its demethylation in presence of benzene over aluminosilicates.

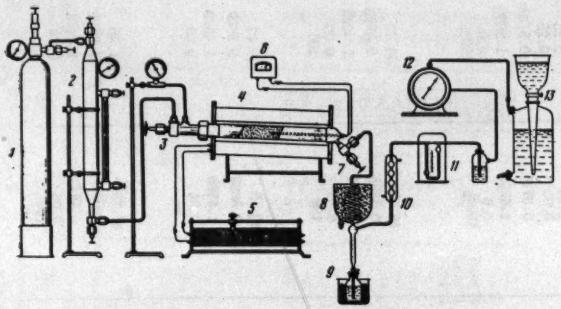


Fig. 1. Laboratory flow-type apparatus for reactions under pressure: 1) nitrogen cylinder; 2) reservoir of raw material; 3) reactor; 4) tube furnace; 5) rheostat; 6) galvanometer; 7) reduction valve; 8) refrigerated condenser; 9) receiver; 10) gas condenser; 11) flowmeter; 12) gas meter; 13) gas holder.

The experiments were carried out in the laboratory flow-type reaction apparatus shown diagrammatically in Fig. 1.

Our raw materials were "pure for cryoscopy" coal-tar benzene (b.p. 79.74-80.10°; bromine value 0.03; density 0.8782; refractive index 1.5010; sulfonatables 99.6%) and o-xylene having b.p. 143-144°; d_4^{20} 0.8800; n_D^{20} 1.5050; sulfonatables 100%. By the oxidation method it was shown that the "o-xylene" contained 98.7% of o-xylene and 1.3% of m-xylene.

Demethylation and Isomerization of o-Xylene in presence of Benzene

Experiments were carried out on the demethylation of o-xylene with associated methylation of benzene. In treatments of a mixture of these hydrocarbons over a synthetic aluminosilicate, in addition to the main reaction of toluene formation, isomerization of o-xylene was observed. The most characteristic results are given in Table 1.

The effects of temperature, pressure, and other factors were studied and the optimum values of the parameters for toluene formation were established. For a single passage of a mixture of o-xylene and benzene at a molar ratio of 1 : 2, a pressure of 5 atm, a temperature of 525°, and a rate of 0.5 : 1, the yield of catalyzate was 97.1%, and 0.9% of coke and 0.8% of gas were obtained. In the course of the process, part of the benzene was alkylated to toluene, and its content fell from 58% in the original mixture to 49.4% in the catalyzate.

A considerable fraction of the o-xylene was demethylated to toluene, so that the content of the xylene fraction fell from 34.9 to 17.7%. The rest of the o-xylene was isomerized to m- and p-xylenes. The boiling range of the xylene fraction was lowered appreciably, and there was a corresponding reduction in density and refractive index. Increase in pressure to 15 atm directed the process toward maximum formation of toluene. Its content in the catalyzate was increased to 27-28%. The yields of catalyzate, coke, and gas (percent by weight on original mixture) varied over the ranges 94.3-95.2%, 1.9-2.2%, and 1.7-2.3%, respectively. Spectrum analysis of the xylene fraction of the catalyzate showed that it contained 16% of o-xylene, 38% of m-xylene, 23% of p-xylene, and 20% of ethylbenzene.

Our results give us reason to suppose that in the catalytic treatment of a mixture of o-xylene and benzene the demethylation reaction is preceded by the isomerization of o-xylene. The p-xylene formed is fairly readily dealkylated under the conditions of the experiment with formation of toluene. The reaction of dealkylation of xylene with associated alkylation of benzene proceeds over aluminosilicates without any accompanying decomposition or condensation side reactions. The formation of unsaturated hydrocarbons and high-boiling condensation products is not observed. The iodine value of the catalyzate is zero, and its sulfonatable content is 100%. The bromine value of the toluene isolated from the catalyzate is 0.03, its density varies in the range 0.8665-0.8670, and its refractive index is 1.4969-1.4972.

On the basis of the values of the conversions of benzene and xylene and of the yields of toluene and trimethylbenzenes we calculated the relative contributions of the reactions taking part in the formation of toluene. The results are given in Table 2.

For temperature 525°, rate 0.5 : 1, duration of reaction cycle 50 minutes, and pressure 15 atm, the contributions of the reactions of dealkylation of xylene and associated alkylation of benzene in the formation of toluene are almost equal and vary in the range 44-47%. The contribution of the disproportionation of xylene is 9-10%. In the catalytic treatment of a mixture of o-xylene and benzene, in addition to these reactions and the reaction of redistribution of hydrogen, the hydrogenolysis of one methyl group of xylene with formation of toluene and methane may occur to a small extent. Analysis showed that the gaseous reaction products consisted mainly of a mixture of methane and hydrogen.

TABLE 2

Main Characteristics of the Catalytic Treatment of a Mixture of o-Xylene and Benzene over Synthetic Aluminosilicate Catalysts

Experimental conditions				Demethylation and assoc. methylation				Redist. of CH_3 groups (dispropor. of xylene)		Consumption of xylene	
				Amount of toluene formed							
				by methylation of benzene		by demethylation of xylene		by dispropor. of xylene			
Temperature (°C)	Pressure (atm)	Rate (vol. of raw mater. per 1 vol. of catalyst/hr)	Duration of cycle (min)	(g)	% of total yield of toluene)	(g)	(% of total yield of toluene)	(g)	% of total yield of toluene)	On demethylation and dispropor. (g)	Conversion of xylene (g)
525	15	0.5 : 1	50	12.61	45.7	12.05	43.7	2.91	10.6	20.59	23.38
25	15	0.5 : 1	50	13.57	47.3	12.47	43.5	2.63	9.14	20.45	23.73

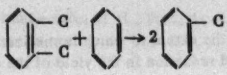
TABLE 3

Isomerization of o-Xylene over an Aluminosilicate

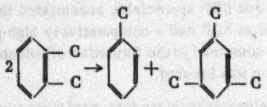
Characteristics of experiment	o-Xylene	Pressure 1 atm; rate 0,5 : 1, duration of cycle 30 minutes			
		400°	450°	500°	525°
Material balance sheet (% by wt.)					
Catalyzate	—	97.90	97.59	97.19	96.53
Gas	—	0.57	0.90	1.10	1.41
Coke	—	0.02	0.12	0.27	0.35
Losses	—	1.43	1.38	1.43	1.49
Characteristics of Catalyzate					
Start of boiling (°C)	139.5	107	105	106	106
To 108	—	—	0.50	0.80	0.92
From 108 to 113	—	1.20	1.80	4.60	6.12
From 113 to 118	—	0.63	1.76	0.90	0.94
From 118 to 125	—	0.50	1.40	0.94	0.90
From 125 to 132	—	0.98	1.76	0.92	0.86
From 132 to 136	—	0.80	1.70	0.98	0.90
From 136 to 140	1.33	58.55	69.16	65.08	54.00
From 140 to 146	91.73	30.18	9.90	7.96	14.52
From 146 to 150	—	0.85	1.80	2.96	2.20
From 150 to 160	—	2.08	3.06	4.80	4.96
From 160 to b.p.	—	—	2.70	3.80	9.00
End of boiling (°C)	144.2	158	163	164	163.7
Total Yield (% by weight)	93.06	94.77	95.54	93.74	95.32
Residue (% by weight)	4.46	3.75	3.05	4.97	3.65
Losses (% by weight)	2.48	1.48	1.41	1.29	1.03
d_4^{20}	0.8803	0.8702	0.8715	0.8693	0.8702
n_D^{20}	1.5055	1.4985	1.5003	1.5003	1.5001
Characteristics of Fractions					
136-140° fraction					
Yield (% by weight of catalyzate)	1.33	58.55	69.16	65.08	54.0
d_4^{20}	0.8802	0.8715	0.8696	0.8659	0.8681
n_D^{20}	1.5052	1.4990	1.4994	1.4988	1.4990
Chemical Composition					
o-Xylene	98.7	29.0	30.3	34.5	27.8
m-Xylene	1.3	48.8	47.1	42.0	46.3
p-Xylene	—	22.2	22.6	23.5	25.9
140-146° fraction					
Yield (% by weight of catalyzate)	91.06	30.18	9.90	7.96	14.52
d_4^{20}	0.8800	0.8799	0.8785	—	—
n_D^{20}	1.5051	1.5045	1.5022	—	—
108-113° fraction					
Yield (% by weight of catalyzate)	—	1.20	1.80	4.60	6.12
d_4^{20}	—	—	—	0.8665	0.8673
n_D^{20}	—	—	—	1.4968	1.4965

The catalytic treatment of a mixture of o-xylene and benzene over aluminosilicates under optimum conditions for toluene formation is characterized by the simultaneous occurrence of the following main reactions:

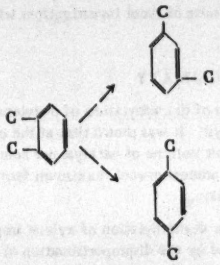
1) Demethylation of xylene with associated methylation of benzene:



2) Redistribution of methyl groups by disproportionation of xylene:



3) Isomerization of o-xylene with formation of m- and p-xylenes:



The formation of ethylbenzene probably occurs as a result of the alkylation of benzene by fragments formed in the decomposition of the coke-forming macromolecular condensation products.

Isomerization of o-Xylene

A series of experiments was carried out on the isomerization of o-xylene over a synthetic aluminosilicate catalyst. The effects of pressure and temperature were studied, and their optimum values for the isomerization process were determined. The xylene fractions obtained were analyzed by Ullmann oxidation [12]. The xylene fractions of catalyzates obtained in experiments carried out under optimum conditions were subjected to spectrum analysis. Also, the mixtures of phthalic acid and its isomers obtained in the oxidation were investigated by x-ray analysis [13].

Our experimental results showed that the application of pressure accelerates the disproportionation of xylene. As a result, with increase in pressure the contents of toluene and trimethylbenzenes in the reaction product increase appreciably. At atmospheric pressure in the temperature range 400-450° the process consists mainly in the isomerization of xylene. The results of experiments on the isomerization of o-xylene are given in Table 3.

At 400° at a rate of feed of 0.5, a single passage of o-xylene over the catalyst results in the formation of 97.9% of catalyzate, 0.6% of coke, and 0.02% of gas. The lower boiling limit of the catalyzate was 107°, and

the upper was 158°. The toluene content of the catalyzate was 1.2%. A considerable proportion of the o-xylene was isomerized and passed into the fraction boiling over the range 136-140°. Thus, the yield of this fraction was increased from 1.3% in the raw material to 58.5% in the catalyzate. There was a corresponding lowering of the density of the catalyzate from 0.8803 to 0.8702, and the refractive index was lowered from 1.5055 to 1.4985. Analysis of the fraction by the oxidation method indicated that it contained 29.0% of o-xylene, 48.8% of m-xylene, and 22.2% of p-xylene.

Rise in temperature to 450° increased the extent to which isomerization occurred. The yield of the 136-140° was increased to 69%. There was a marked reduction in the yield of the o-xylene fraction (9.9%). The disproportionation of xylene proceeded somewhat more vigorously, and the yields of the toluene and trimethylbenzene fractions therefore increased. The contents of o-, m-, and p-xylenes in the 136-140° fraction were 30.2, 47.1, and 22.6%, respectively. Analysis of this fraction by the Raman-spectrum method indicated contents of 35, 43, and 22%, respectively.

Further rise in temperature to 500° and 525° appreciably accelerated the reaction of disproportionation of methyl groups. The catalyzate obtained at 525° had a comparatively high p-xylene content, but a considerable proportion of the original o-xylene was consumed in the formation of toluene and trimethylbenzenes, so that, on the whole, the extent of isomerization was lowered.

These results on the analysis of catalyzates indicate that maximum isomerization of o-xylene into p- and m-xylenes over synthetic aluminosilicates is attained at atmospheric pressure in the temperature range 450-500°.

Considerable practical interest is presented by the isomerization of m-xylene. The large available supplies of this compound open up wide possibilities for the industrial development of p-xylene manufacture. Our investigations show that the maximum effect in the isomerization of m-xylene is attained in the temperature range 400-450° under vacuum conditions. The results of these investigations will be published in our next communication.

SUMMARY

1. An investigation was made of the reaction of demethylation of o-xylene with associated methylation of benzene over a synthetic aluminosilicate catalyst. It was shown that at the optimum temperature of 525°, at a rate of feed of 0.5 volume of o-xylene per unit volume of catalyst per hour, and for a reaction cycle of 50 minutes the application of pressure directs the process toward maximum formation of toluene, the yield of which comprises 27-28% on the amount of catalyzate.

2. In the formation of toluene, not only is the demethylation of xylene important, but also the associated methylation of benzene. A little toluene is formed by the disproportionation of xylene. o-Xylene undergoes isomerization to a considerable extent with formation of m- and p-xylenes.

3. The isomerization of o-xylene was studied. It was shown that maximum isomerization over a synthetic aluminosilicate catalyst is attained in the temperature range 450-500°. In a single passage of o-xylene, 50-60% of it is converted into p- and m-xylenes. The xylene fraction of the catalyzate contains 22-23.5% of p-xylene.

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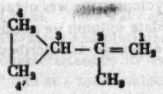
CATALYTIC VAPOR-PHASE HYDROGENATION OF ISOPROPYLCYCLOPROPANE AND ISOPROPENYLCYCLOPROPANE

B. A. Kazansky, M. Yu. Lukina and A. I. Malyshev

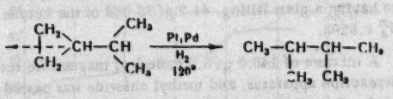
As we have recently shown [1], at room temperature in an alcohol medium in presence of platinum or palladium black, the three-membered ring of isopropylcyclopropane does not undergo hydrogenolysis. On the other hand, under the same conditions and with the same catalysts isopropenylcyclopropane undergoes complete or partial hydrogenolysis. Thus, in presence of palladium black [2] two molecules of hydrogen add to one isopropenylcyclopropane molecule with formation of 2-methylpentane, and in presence of platinum black [1] addition of 1.3 molecules occurs with formation of a mixture consisting of 30% of 2-methylpentane and 70% of isopropylcyclopropane. It should be noted that isopropenylcyclopropane remains unchanged when shaken for a long time with a reduced palladium catalyst in absence of hydrogen [2].

The observed rupture of the C–C bond adjacent to the substituent in the three-membered ring in the hydrogenation of isopropenylcyclopropane is not in accord with various cases described in the literature in which, almost without exception, hydrogen, reacting with an alkylcyclopropane in presence of catalysts adds at the C–C bond lying opposite to the substituent [3-5]. This fact prompted us to suggest that the cause of the different course of the hydrogenolysis of the three-membered ring in isopropenylcyclopropane is the conjugation of the ring with the double bond of the side chain, which lowers the stability of the C–C bonds (3,4 and 3,4') adjacent to the substituent:



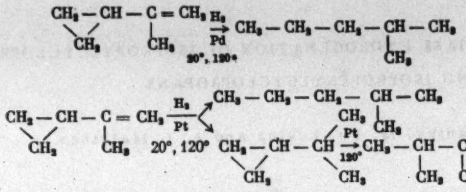
It must be pointed out that in the cases described in the literature the catalytic hydrogenolysis of alkylcyclopropanes was not carried out under the conditions indicated above, but at a higher temperature (70-150°) and without solvent. In the present investigation, therefore, we studied the vapor-phase hydrogenolysis of both isopropyl- and isopropenyl-cyclopropanes in presence of platinum and palladium, the experimental conditions being identical for the two hydrocarbons.

It was found that isopropylcyclopropane was completely hydrogenolyzed at 120°* and at a space velocity of 0.2 with formation, irrespective of which catalyst was used, of only 2,3-dimethylbutane, the product of the rupture of the C–C bond lying opposite to the substituent:

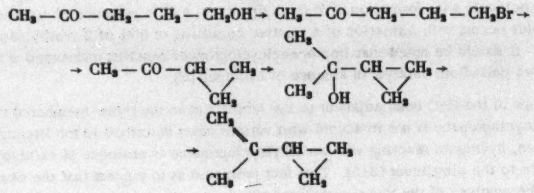


* Hydrogenolysis proceeds also at lower temperatures of 80° upwards.

Experiments on the hydrogenation of isopropenylcyclopropane under the same conditions showed that, as in liquid-phase hydrogenation at room temperature, the composition of the catalyzate depends on the identity of the catalyst. Over palladized charcoal, 2-methylpentane is again the only hydrogenation product, whereas in presence of platinized charcoal a mixture of 2-methylpentane and 2,3-dimethylbutane is obtained, the latter being formed evidently as a result of hydrogenolysis at this temperature of the isopropylcyclopropane first formed:



Isopropenylcyclopropane was prepared as follows [6]:



Isopropylcyclopropane was prepared by the hydrogenation of isopropenylcyclopropane in presence of a copper-chromium catalyst. However, in spite of Slabey's results [7], we did not succeed in preparing the pure hydrocarbon by this method. In all cases isopropylcyclopropane was obtained in admixture with 2-methylpentane. After distillation of the mixture through a 70-plate column we obtained isopropylcyclopropane which we estimated to have a purity of about 97%. All the experiments described below were carried out with the preparation.

EXPERIMENTAL

5-Bromo-2-pentanone. A mixture of 204 g (2.0 moles) of 5-hydroxy-2-pentanone (b.p. 103-108° (20 mm); n_D^{20} 1.4395) and 600 ml of 55% hydrobromic acid (sp. gr. 1.59) was prepared at room temperature. After ten hours the reaction mixture was poured into four times its volume of water. The bromo compound was extracted three times with ether. The extract was dried, ether was distilled off, and the reaction product was fractionated. It gave 220.0 g (63.0%) of 5-bromo-2-pentanone, b.p. 76-77° (10 mm); n_D^{20} 1.4693; d_4^{20} 1.3895.

Cyclopropyl Methyl Ketone. Water (10 ml) was added to 100 g (0.6 mole) of freshly distilled 5-bromo-2-pentanone, and the mixture was shaken vigorously while 48.0 g (1.17 moles) of potassium hydroxide powder was added in small portions. Reaction was exothermic and was complete within a few minutes. Water was added, and the ketone was steam-distilled off, salted out with potassium carbonate, separated, and dried. After distillation through a 30-plate column having a glass filling, 44.2 g (76.0%) of the ketone was obtained; b.p. 112.8-113.0° (760 mm); n_D^{20} 1.4248; d_4^{20} 0.8993.

2-Cyclopropyl-2-propanol. A mixture of 146.0 g (6.0 moles) of magnesium turnings and 500 ml of absolute ether was prepared in a Grignard-reaction apparatus, and methyl chloride was passed in from a cylinder until most of the magnesium had reacted. The mixture was warmed and stirred for one hour, and was then cooled to +5° in a current of nitrogen. At this temperature, a solution of 420.0 g of distilled cyclopropyl methyl ketone in

1 liter of absolute ether was added. The mixture was heated for eight hours at the boiling point of ether. It was then cooled and poured onto ice.* After extraction and drying, ether was distilled off, and the alcohol was distilled through a 30-plate column having a glass filling. The product, amounting to 298.0 g (60%), had b.p. 123.5-123.7° (760 mm); n_D^{20} 1.4333; d_4^{20} 0.8792.

Isopropenylcyclopropane. 2-Cyclopropyl-2-propanol (99.2 g, i.e., 1.0 mole) was heated with 2 drops of concentrated sulfuric acid in a flask fitted with a column having a glass filling. The isopropenylcyclopropane then formed was distilled off, washed with water, dried and boiled over sodium. Fractionation through a 40-plate column gave 60.0 g (74%) of isopropenylcyclopropane, b.p. 70.5° (760 mm); n_D^{20} 1.4255; d_4^{20} 0.7517; The literature [8] gives b.p. 70.33° (760 mm) n_D^{20} 1.42550; d_4^{20} 0.75153.

Isopropylcyclopropane. A mixture of 82.8 g (1.0 mole) of isopropenylcyclopropane, 62 ml of distilled ethanol, and 8.3 g of copper-chromium catalyst prepared by the method described in the literature [9] was prepared in a 500-ml autoclave. The hydrogenation went at 100-130° under a pressure of hydrogen of 105-140 atm. Absorption of hydrogen was observed only after 6-8 hours' heating, and it was complete in 48 hours. The reaction product was separated from the catalyst and distilled. After being washed with water it was boiled over the sodium and distilled through a 60-plate column. The results of the fractionation are given in Table 1.

TABLE 1

Fraction	B.p. (°C)	Amount (g)	n_D^{20}	d_4^{20}	Aniline point (°C)
I	54.2—58.4	2.9	1.3840	—	—
II	58.4	18.1	1.3859	0.6968	34.9
III	58.4- 58.5	17.1	1.3854	0.6958	—
IV	58.5—58.6	7.4	1.3852	—	—
V	Residue	20.0	1.3775	—	—
	Losses	2.4	—	—	—

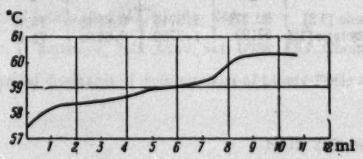
Fraction II was isopropylcyclopropane in admixture with about 3% of 2-methylpentane. For isopropylcyclopropane the literature [8] gives b.p. 58.37° (760 mm); n_D^{20} 1.38639; d_4^{20} 0.69829.

Vapor-phase Hydrogenation of the Hydrocarbons. This was carried out in a flow system by the procedure described previously [4]. The catalysts were palladized and platinized charcoals prepared according to Zelinsky and Turova [10]. The platinized charcoal wascharacterized by its behavior in the ring-opening of cyclopentane [11]. After the passage of cyclopentane at 300° and at a space velocity of 1.0, the catalyzate contained 55% of pentane. The results of the hydrogenation experiments are given in Table 2.

The results of the fractionations of the catalyzates of Series I, II, and III are given in Table 3.

Data in the literature on the constants of 2-methylpentane and 2,3-dimethylbutane are given in Table 4.

It will be clear from a comparison of the data in Tables 3 and 4 that the hydrogenation of isopropylcyclopropane (Series I and III) over platinized and palladized charcoal gives 2,3-dimethylbutane, the constants of which differ a little from the reported values owing to a little 2-methylpentane impurity in the original isopropylcyclopropane, whereas hydrogenation of isopropenylcyclopropane over palladized charcoal (Series II) gives 2-methylpentane. The catalyzate from Series IV was fractionated through a 30-plate column having a copper filling. The results of the fractionation are given in Table 5 and in the figure.



*About 400 ml of glacial acetic acid was added to 2-3 kg of ice.

TABLE 2

Catalyst	Series of experiments*	Hydrocarbon	Temperature (°C)	Space velocity (hour^{-1})	n_D^{20}
Pd on charcoal (10 ml, i.e., 2.7 g)	I	Isopropylcyclopropane	150	0.2	1.3743
			120	0.2	1.3743
			80	0.2	1.3743
			70	0.2	1.3743
	II	Isopropenylcyclopropane	120	0.2	1.3713
			120	0.2	1.3713
			120	0.2	1.3713
Pt on charcoal (10 ml, i.e., 2.9 g)	III	Isopropylcyclopropane	150	0.2	1.3743
			120	0.2	1.3743
			80	0.2	1.3743
			70	0.2	1.3750**
	IV	Isopropenylcyclopropane	120	0.2	1.3731
			120	0.2	1.3731***

*All the catalyzates from the experiments of a given series were combined and fractionated.

**The catalyzate obtained at 70° was not added to the catalyzates of the other experiments of this series.

***12.0 ml of catalyzate was collected.

TABLE 3

Series of experiments	Amount of substance (g)	B.p. in °C p in mm	n_D^{20}	d_4^{20}	Aniline point (°C)
I	5.4	57.3—57.7 (742.5)	1.3742	0.6598	72.2
II	4.1	58.5—58.8 (733.2)	1.3713	0.6530	73.7
III	3.9	57.1—57.5 (742.3)	1.3743	0.6600	72.0

TABLE 4

Hydrocarbon	B.p. (°C)	n_D^{20}	d_4^{20}	Aniline point (°C)
2-Methylpentane [12]	60.271	1.3715	0.6532	74.6
2,3-Dimethylbutane [12]	57.99	1.3750	0.6616	71.9

The substance fractionated amounted to 12.0 ml (7.9 g) and had n_D^{20} 1.3731 and d_4^{20} 0.6575. Toward the end of the distillation 10 ml of heptane was added as a displacer.

TABLE 5

Fraction	Temperature (°C at 760 mm)	Amount (g)	n_D^{20}	d_4^{20}	Aniline point (°C)
I	57.6—58.5	1.6	1.3752	0.6634	70.6
II	58.5—58.8	1.4	1.3739	0.6599	—
III	58.8—60.3	3.3	1.3722	0.6563	—
IV	60.3—60.4	0.7	1.3712	0.6532	73.9
	Losses	0.9			

The data in the figure and in Table 5 enable us to conclude that the catalyzate from Series IV experiments is a mixture of approximately equal amounts of 2-methylpentane and 2,3-dimethylbutane, which could not be resolved in the column used owing to the closeness of the boiling points of these hydrocarbons.

SUMMARY

1. A study was made of the hydrogenation of isopropyl- and isopropenyl-cyclopropanes over palladized and platinized charcoals at 120° at a space velocity of 0.2.

2. Substantial differences were found in the behaviors of the two hydrocarbons in the reaction of catalytic hydrogenation: irrespective of the identity of the catalyst, isopropylcyclopropane is converted into 2,3-dimethylbutane; in presence of palladium isopropenylcyclopropane is converted into 2-methylpentane, and in presence of platinum it is converted into a mixture of 2-methylpentane and 2,3-dimethylbutane.

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KINETICS OF THE DEHYDROGENATION OF ISOPROPYL AND ETHYL ALCOHOLS OVER MANGANOUS OXIDE

A. A. Tolstopyatova, A. A. Balandin and E. M. Dmitriev

Manganous oxide is a good, cheap catalyst for the ketonization of acids. As Sabatier and Maihle showed [1], fatty acids are decarboxylated over MnO at 400-450° with formation of ketones in good yield; e. g., adipic acid gives cyclopentanone. Zelinsky and Ryakhina [2] effected the ketonization of naphthenic acids over manganous oxide. There are also various papers [3] on the dehydrogenation of alcohols over MnO, and in these it is shown that dehydrogenation proceeds without side reactions, although MnO has lower activity than copper and other catalysts. We were the first to make a kinetic investigation of the dehydrogenation of alcohols over manganous oxide: one of us [4] investigated the rate of dehydrogenation of cyclohexanol, and in the present investigation we have studied the kinetics of the dehydrogenation of ethyl and isopropyl alcohols.

EXPERIMENTAL

a) Apparatus. The kinetic experiments were carried out in the usual flow apparatus with automatic feed. The volume of gas formed was measured in a eudiometer having a constant lower level; the measurement was accurate within 0.5 ml. The end of the pocket of the chromel-alumel thermocouple was in the middle of the catalyst layer. The temperature was registered on a potentiometer accurately within 0.5°. The reactor was a quartz tube, 16 mm in diameter. It was connected by means of ground joints to an automatic spray and to a receiver, which was fitted with a water-cooled reflux condenser.

b) Starting Substances. Commercial ethyl alcohol was distilled through a column and then had d_4^{15} 0.8118, which corresponds to 93.93% by weight or 94.0 mole % of alcohol. Isopropyl alcohol was rendered absolute by boiling it for 20 hours with quicklime and distilling it through a column. The fraction used in the experiments had b.p. 81.5-82° (75 mm), n_D^{20} 1.5782 and d_4^{20} 0.7867 (the literature [5] gives n_D^{20} 1.5770 and d_4^{20} 0.7870). Acetone used for the preparation of binary mixtures with isopropyl alcohol was purified by boiling it for six hours with potassium permanganate, distilling through a column, and redistilling over anhydrous potassium carbonate. The acetone so obtained had the following constants: 56° (752 mm); n_D^{20} 1.3590; d_4^{20} 0.7920 (the literature gives n_D^{20} 1.3583 [6] and d_4^{20} 0.7906 [7]).

Binary mixtures of isopropyl alcohol and acetone were prepared by mixing the appropriate volumes of isopropyl alcohol and acetone; they contained 24.98, 49.32 and 73.75 mole % of $(CH_3)_2CHOH$. As the differences in density between the mixtures were very small, the rate of passage was the same for all of the mixtures. The required mole-percentage compositions of the mixtures with hydrogen were attained by changing the rates of feed of alcohol and the current in the electrolyzer. For each mixture, the necessary current strength was calculated from Faraday's law. The amount of hydrogen evolved was checked with the aid of the eudiometer so as to ensure the absence of complications. Hydrogen was obtained by the electrolysis of sodium hydroxide solution; it was purified from oxygen over palladium and dried with sulfuric acid.

c) Catalysts. Manganous oxide was prepared from manganese nitrate ("Chemically Pure Brand") and crystalline sodium carbonate ("Pure"). A saturated solution of manganese nitrate was added dropwise to a stirred 10% solution of crystalline sodium carbonate; the latter was in excess (5% more than the calculated amount). The mixing of the solutions was carried out at 45°. The white precipitate of manganese carbonate was washed with distilled water by decantation until a test for nitrate (with diphenylamine in sulfuric acid) was negative; it was filtered off and pressed out between filter papers on a pipe-clay tile.

The paste of manganous carbonate was placed in a glass tube, 35 mm in diameter, and heated in an electric furnace in an atmosphere of nitrogen at 200° for three hours (until the liberation of water ceased). The tube was cooled, and the manganese carbonate was placed in the quartz reaction tube and decomposed at 400° for four hours in a current of dry nitrogen. The completeness of the decomposition of the carbonate was determined by the absence of carbon dioxide in the exit gases. In order to create a reducing atmosphere, methanol was first used. Doubly distilled commercial methanol was passed into the reaction tube from a spray at the rate of 0.2 ml per minute at 400°. This method of reduction to MnO was used in all the above-mentioned investigations with this catalyst [1-3].

We found that in the decomposition of manganese carbonate, methanol can be successfully replaced by hydrogen. Also, hydrogen is able to restore the activity of the catalyst when it is not too strongly poisoned. In further work the decomposition was always carried out in a stream of electrolytic hydrogen purified from oxygen and dried at the temperature of the experiment (350-420°) until water ceased to separate (two hours). In the early experiments the catalyst was used in powder form, but is rapidly dispersed. In further work we used a molded catalyst. Such a catalyst is pale green, but immediately becomes brown when brought into contact with air. The oxidation of manganous oxide is highly exothermic, and there is therefore, a sharp rise in temperature in the first minutes of passage of air in the regeneration of the catalyst.

d) Experimental Procedure. After being reduced in the reaction tube, the catalyst did not again come into contact with air: during and after the experiments it was in an atmosphere of nitrogen, hydrogen, or alcohol vapor. During the heating of the furnace, the catalyst was in a stream of nitrogen. When the required temperature was reached, the nitrogen was turned off and the reactant was sprayed into the reactor. After the establishment of a stationary state, regular readings were taken (ml) of the amount of gas that had separated. The experiment continued for 30-35 minutes. In the interval between experiments hydrogen was passed, but before the beginning of the next experiment the hydrogen was replaced by nitrogen. The volume of gas separating was reduced to the standard state. The gas was analyzed in a VTI apparatus. We shall now consider the results for ethyl and isopropyl alcohols separately.

Dehydrogenation of Ethyl Alcohol

The experiments on the dehydrogenation of ethyl alcohol were carried out in the temperature range 295-400°. The rate of passage of alcohol was 0.2 ml per minute. In all, 80 experiments were carried out with four portions of the same catalyst; in Experiments 1-45 the length of the catalyst layer was 15 cm and the catalyst was reduced with methanol, but in Experiments 46-80 the length of the catalyst layer was 7.5 cm and the catalyst was reduced with hydrogen. The activity of the catalyst was constant for 15-20 experiments, but after 8-10 hours' work, its activity fell and we were unable to restore its original activity. The gas separating contained 70-95% of hydrogen, 1-12% of unsaturated hydrocarbons, 4-10% of carbon dioxide, 1-5% of carbon monoxide, and 0.5-2% of saturated hydrocarbons. With rise of temperature the amount of gas separating increased. However, the hydrogen content of the gas fell and the contents of unsaturated hydrocarbons and carbon dioxide simultaneously rose.

Figure 1 shows the dependence of gas composition on temperature. From this graph and the total amount of gas separating in 3 minutes (STP) we calculated the values of m (amount of hydrogen (ml) in 3 minutes at STP). Figure 2 shows the dependence of the extent of conversion of alcohol on temperature. Hydrogen used for hydrogenation is not taken into account owing to the low content of saturated hydrocarbons. For each new portion of catalyst the activation energy was determined (ε_1 for the first portion, ε_2 for the second, and so on). These results are given in Table 1 and Figures 3-6.

The activation energy ε was calculated from the formula

$$\varepsilon = \frac{4.575\,(\lg m_1 - \lg m_2)}{\frac{1}{T_2} - \frac{1}{T_1}}. \qquad (1)$$

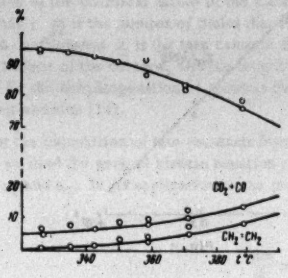

Fig. 1

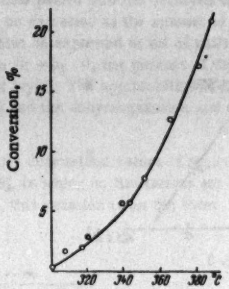

Fig. 2

The determination of the activation energy gave the mean value of 29,500 cal/mole. The points fit satisfactorily to straight lines. The value of the activation energy was the same in Experiments 46-66 (Fig. 6) as in Experiments 11-45, in spite of the fact that the catalyst layer was half the length in the first series. Straight

TABLE 1

Experiment	Temperature (°C)	m	Experiment	Temperature (°C)	m	Experiment	Temperature (°C)	m	Experiment	Temperature (°C)	m
11	307.5	2.9	25	359.5	16.6	44	343	2.7	46	343	2.8
12	317.7	4.5	28	359.5	15.2	37	359.5	5.9	50	350	4.2
20	317.7	3.8	29	371.5	24.2	42	359.5	6.5	57	359.5	6.2
13	326.5	6.6	31	371.5	26.8	38	371.5	7.7	63	359.5	6.2
17	326.5	6.3	33	371.5	22.2	41	371.5	8.5	62	371.5	7.8
18	326.5	6.4	27	388.5	44.4	43	371.5	8.0	64	371.5	9.5
24	343	12.6	30	388.5	44.6	40	388.5	15.1	67	380	12.2
16	343	12.5	32	388.5	44.2	39	400	26.5	66	388.5	14.4
15	359.5	23.1									
19	359.5	24.6									
21	359.5	24.5		$\varepsilon_2 = 30\,600$			$\varepsilon_3 = 29\,400$			$\varepsilon_4 = 29\,500$	

$\varepsilon_1 = 29\,300$

lines were obtained in Figures 3, 4 and 5. In Figure 6 there is appreciable curving of the line at higher temperatures. This indicates that the dehydrogenation of ethyl alcohol does not proceed according to a zero-order law. For the establishment of the kinetic equation it was necessary to determine the relative adsorption coefficients of the reaction products, the true rate constants, and the true activation energies, and this was done for isopropyl alcohol. The dehydrogenation reaction proceeds smoothly without formation of by-products. We observed that a completely oxidized catalyst also has catalytic activity toward ethyl alcohol. The results of two experiments with an oxidized catalyst are given in Table 2.

There is a reference in the literature to the dehydrogenation of ethyl alcohol over manganic oxide [8].

Dehydrogenation of Isopropyl Alcohol

a) Determination of the Rate of Dehydrogenation. The experiments were carried out in the temperature

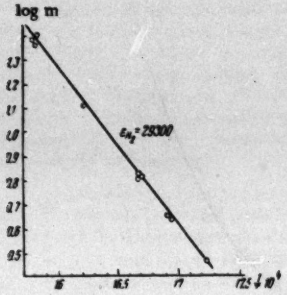

Fig. 3

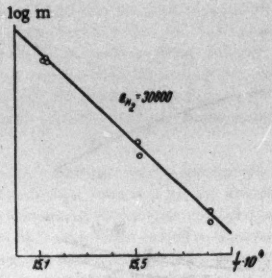

Fig. 4

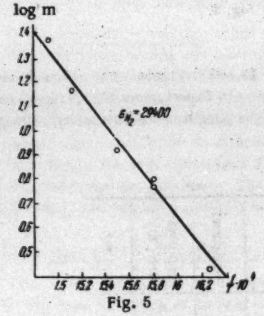

Fig. 5

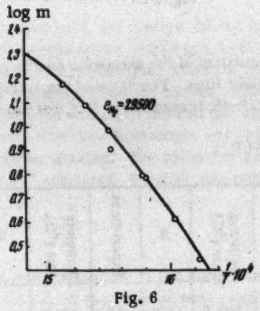

Fig. 6

range 300-400°. The length of the catalyst layer was 7.5 cm. The rate of passage of alcohol was 0.15 ml/minute. The results are given in Table 5 (Columns 1-3). The determination of true rate constants and true activation energies from these data requires the determination also of the relative adsorption coefficients of the reaction products, hydrogen and acetone.

TABLE 2

Catalyst	Experiment	Temperature of experiment (°C)	Gas analysis (%)				
			H_2	Unsaturated hydrocarbons	Saturated hydrocarbons	CO_2	O
Reduced	77	343	94	1	0.5	4.5	0
Oxidized	78	343	70	1.5	3.5	2.5	0

b) Method of Determining the Constants.

Balandin [9] proposed a kinetic method of determining relative adsorption coefficients experimentally. Later, in a paper by Bork and Balandin [10] on the kinetics of the dehydrogenation of ethyl and propyl alcohols over copper, the equation

$$k = \frac{N \cdot m}{N - \frac{m}{2}} \qquad (2)$$

was derived for the case in which the relative adsorption coefficient of one of the products α_2/α_1 is unity, and that of the other α_3/α_1 is zero (cf. [11]). This Equation was extended [12] to the case when the sum of the coefficients is unity, $\alpha_2/\alpha_1 + \alpha_3/\alpha_1 = 1$, and the equation

$$\alpha_2/\alpha_1 = \frac{kM - m(k/2 + M)}{m(N - M)}, \qquad (3)$$

was derived in which M is the amount of the original substance (moles) passed into the catalysis tube (M may be expressed also as the amount of gas (ml) that would be formed if the whole of the original reactant underwent the reaction); N is the total amount of substance (moles) passed into the catalysis tube in unit time, irrespective of the chemical nature of the molecules (N may be expressed as the amount of gas (ml) that may be formed); m is the number of moles that react (m may also be expressed as ml of gas); α_1 and α_2 are adsorption coefficients; k is the rate constant for the reaction $k = k_1 \cdot \omega$, the product of the rate constant, the active surface of the catalyst, and the length of the catalyst layer. The applicability of Equations 2 and 3 was proved for the dehydrogenation of alcohols over copper [13] and the dehydrogenation and dehydration of alcohols over alumina [14].

For the calculation of rate constants from experimentally determined values of m, in the present investigation we used the general kinetic equation of Balandin [15], in which no limitations are imposed on the values of α_1, α_2 and α_3. In its application to the present reaction, this equation takes the form

$$\frac{dm}{d\tau} = k \frac{A_1 - m}{A_1 + (z_2 + z_3 - 1)\, m} \tag{4}$$

or after integration

$$k = (z_2 + z_3)\, A_1 \cdot \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1)\, m, \tag{5}$$

in which k is the rate constant (k is expressed in different units in Equations 4 and 5); m is the number of moles of substance that reacts in unit time (milliliters of hydrogen liberated in 3 minutes); A_1 is the number of moles of the original substance entering the tube in unit time (milliliters of gas which would be formed in three minutes if the substance reacted completely); z_2 and z_3 are relative adsorption coefficients.

The calculation of relative adsorption coefficients was carried out by the formula [16]

$$z_2 = \frac{2B_1\, H - B_1 Y - HY}{(1 - B_1)\, Y}, \tag{6}$$

in which

$$Y = \frac{m}{\Sigma A_r}; \quad B_1 = \frac{A_1}{\Sigma A_r}; \quad H = \frac{kl}{2\Sigma A_r}; \quad H = \frac{Y_0}{2 - Y_0}.$$

For experiments with the pure reactant Equation 6 is identical with Equation 3, for $Y = \frac{m}{N}$; $B_1 = \frac{M}{N}$; $H = \frac{k}{2N}$; $z_2 = \frac{\alpha_2}{\alpha_1} \Sigma\nu_r$ ($\Sigma\nu_r$ is the sum of the stoichiometric coefficients).

Equation 6 is applicable for the case in which

$$Y_2 \ll \frac{B_1 H}{2\Sigma\nu_r z_r}. \tag{7}$$

The applicability of Equation 5 was proved in a series of investigations [17-21]. Agronomov [17], for the dehydrogenation of isopropyl alcohol over zinc oxide, and Balandin and Klabunovsky [18], for the dehydrogenation of sec. butyl alcohol over nickel, calculated z (the value of which must be substituted in Equation 5

TABLE 3

Isopropyl Alcohol — Hydrogen

Experiment	Temperature (°C)	Amount of alcohol in mixture (mole %)	m found	m calculated from mean z	z calculated by Equation 6 from m found	z calculated from Equation 8
94	317	100	10.6			
96	317	72.5	10.4	10.5	0.07	0.08
98	317	100	10.2			
99	317	46.6	9.9	9.2	0.09	0.02
100	317	46.6	9.7	9.2	0.13	0.04
				Mean	0.10	0.05
83	331	100	15.1			
84	331	72.5	14.7	14.1	0.10	0.12
85	331	100	15.1			
86	331	46.6	12.9	12.9	0.15	0.15
87	331	100	15.1			
88	331	72.5	14.0	14.3	0.19	0.33
89	331	100	15.4			
90	331	46.6	12.8	12.8	0.15	0.17
				Mean	0.15	0.19
119	344.5	100	18.4			
120	344.5	466	14.1	14.1	0.26	0.26
127	359.5	100	28.8			
128	359.5	72.5	26.0	25.8	0.25	0.45
130	359.5	100	29.1			
132	359.5	46.6	20.1	13.3	0.38	0.39
				Mean	0.31	0.42
136	366	100	32.3			
138	366	72.5	30.0	29.9	0.23	0.30
140	366	100	32.7			
141	366	46.6	20.1	26.0	0.50	0.54
				Mean	0.36	0.42

from Equation 6, as we have done. The relative adsorption coefficients required for substitution in Equation 5 may be calculated also from the approximate equation

$$z_r = \frac{m_0/m - 1}{100/p - 1}, \qquad (8)$$

in which m_0 is the number of milliliters of hydrogen formed in the passage of the pure substance, and m is the number of milliliters of hydrogen formed in the passage of a mixture having a mole-percentage content of p. Equation 8 was used for the calculation of z in the papers of Balandin, Bogdanova and Shcheglova [19, 20] on the dehydrogenation of butene, and of Balandin and Isagulyants [21] on the dehydrogenation of cyclohexane, methylcyclohexane, dimethylcyclohexane, tetralin, and methyltetralin over chromic oxide.

c) Determination of Relative Adsorption Coefficients. Experiments with mixtures, which were required for the determination of relative adsorption coefficients, were alternated with experiments with the pure alcohol in order to prove absence of irreversible poisoning. In work with isopropyl alcohol — hydrogen mixtures the catalyst maintained constant activity in the course of the whole series of experiments, and the experiments were

TABLE 4

Isopropyl Alcohol — Acetone

Experiment	Temperature (°C)	Amount of alcohol in mixture (mole %)	$\bar{m}$ found	$\bar{m}$ calculated from mean $\bar{z}$	$\bar{z}$ calculated by Equation 6 from $\bar{m}$ found	$\bar{z}$ calculated from Equation 8
145	331	100	7.9			
146	331	73.75	6.2	6.0	0.80	0.77
148	331	100	8.0			
149	331	49.32	4.1	4.1	0.96	0.93
151	331	100	7.1			
152	331	24.98	1.9	1.9	0.89	0.91
156	331	100	7.8			
157	331	73.75	5.4	5.2	1.23	1.25
161	331	100	7.7			
162	331	49.32	3.9	4.0	0.92	0.97
			Mean		0.92	0.96
170	371.5	100	14.5			
171	371.5	73.75	11.0	11.2	0.99	0.94
172	371.5	100	14.1			
173	371.5	49.32	7.2	7.2	0.96	0.93
175	371.5	100	14.2			
176	371.5	73.75	10.8	10.9	0.93	1.06
			Mean		0.96	0.97
163	399	100	39.3			
164	399	73.75	29.4	29.8	1.02	0.94
165	399	100	39.3			
166	399	49.32	19.7	19.3	0.99	0.96
167	399	100	38.0			
168	399	24.88	8.9	9.1	1.09	1.09
			Mean		1.05	1.00

TABLE 5

Experiment	Temperature of experiment (°C)	m	z	k calculated for $\epsilon = 23,650$	$\log k_0$	Conversion of alcohol (%)
105	317	9.7	11.3	11.0	9.80	7.3
110	331	13.3	17.3	17.0	9.80	10.1
116	344.5	17.9	24.3	25.7	9.76	13.6
115	352	23.9	33.4	33.4	9.80	18.1
126	359.5	27.9	40.6	40.7	9.79	21.2
177	359.5	28.0	40.7	40.7	9.79	21.2
139	386	31.4	47.4	48.2	9.74	23.8
180	388.5	51.5	94.1	93.3	9.8	39.0
178	399	58.0	117.0	123.0	9.76	44.0

Average $\log k_0 = 9.79$; $k_0 = 6.12 \cdot 10^9$; $\frac{\epsilon}{\log_{10} k_0} = 2.42 \cdot 10^3$

therefore carried out one after the other without regeneration of catalyst. The results of these experiments are given in Table 3. In work with mixtures of isopropyl alcohol and acetone, the catalyst was greatly poisoned. Hence, before each experiment the catalyst was regenerated for two hours with air and was then reduced with hydrogen in order to restore its activity. The activity was checked each time in experiments with pure isopropyl alcohol, and the value of the activity found was taken as m_0 for the subsequent experiment with the mixture. The results of experiments on mixtures of isopropyl alcohol and acetone are given in Table 4.

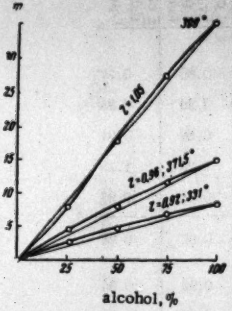

Fig. 7

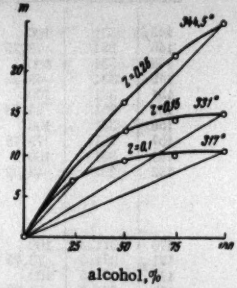

Fig. 8

Figures 7 and 8 show the relationships found between the amount of hydrogen liberated m and the percentage composition of the mixture at various temperatures. Points below the additive straight line correspond to $z > 1$, and points above the straight line correspond to $z < 1$. As will be seen from Figures 7 and 8, for all three temperatures the adsorption coefficients of acetone are very close to unity, but the adsorption coefficients of hydrogen are considerably less than unity and increase with rise in temperature. The relative adsorption coefficients given in Tables 4 and 5 are calculated from Equation 6. Calculation of z from the approximate Equation 8 and, at low temperatures, from Equation 3 gives very similar results. Thus, for Experiment 149 (Table 4) z was calculated from all three equations, and the following values were obtained: Equation 3 gave $z = 0.92$; Equation 6 gave $z = 0.96$; Equation 8 gave $z = 0.97$.

d) Calculation of Reaction-rate Constants and True Activation Energies. The rate constant k was calculated from Equation 5. The values of z_2 and z_3 in Equation 5 were found from the graph in Fig. 9, which expresses the relation between relative adsorption coefficients and temperature. For the calculation of true activation energies we constructed the graph in Fig. 10, in which log k, calculated from Equation 5, is plotted as ordinate and 1/T is plotted as abscissa (Curve 1). The true activation energy was calculated from Equation 1, log m being replaced by log k, and a value of 23,650 cal/mole was found.

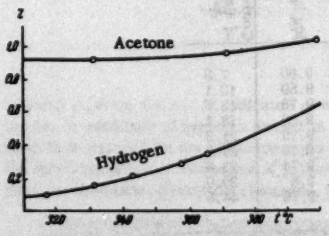

Fig. 9

In Figure 10 Curve 2, obtained from log m, is given for comparison. Table 5 gives the experimental values of m, the rate constants k, and the percentage conversion of the alcohol in the dehydrogenation of isopropyl alcohol.

e) Determination of the Thermodynamic Quantities ΔF, ΔH and ΔS. By the method given previously [22] we may calculate from z (Tables 3 and 4) the changes in free energy ΔF, in heat content ΔH, and in entropy ΔS occurring in the displacement of isopropyl alcohol by acetone and hydrogen from the active centers of manganous oxide:

$$\Delta F = -RT \cdot \ln z;\ \Delta H = \frac{4.57\,(\log z_1 - \log z_2)}{\frac{1}{T_2} - \frac{1}{T_1}};\ \Delta S = \frac{\Delta H - \Delta F}{T}.$$

The results so obtained are given for isopropyl alcohol– hydrogen in Table 6 and for isopropyl alcohol– acetone in Table 7.

TABLE 6

Isopropyl Alcohol– Hydrogen
$\Delta H = 19{,}400$ cal/mole

Temperature (°K)	$z_{hydrogen}$	ΔF (cal/mole)	ΔS $\frac{cal}{(deg \cdot mole)}$
590	0.10	2698	28.3
604	0.15	2275	28.4
617	0.26	1648	28.8
632	0.31	1469	28.4
639	0.36	1297	28.3

TABLE 7

Isopropyl Alcohol– Acetone
$\Delta H = 1690$ cal/mole

Temperature (°K)	$z_{acetone}$	ΔF (cal/mole)	ΔS $\frac{cal}{(deg \cdot mole)}$
604	0.92	99.8	2.6
644	0.96	52.1	2.5
672	1.05	–65.1	2.6

f) Discussion of Results of Experiments on Isopropyl Alcohol. Table 5 gives values of the rate constants k for the dehydrogenation of isopropyl alcohol– as determined, and as calculated from the Arrhenius equation for $\epsilon = 23{,}650$ cal/mole. These values differ very little from one another, which indicates the correctness of

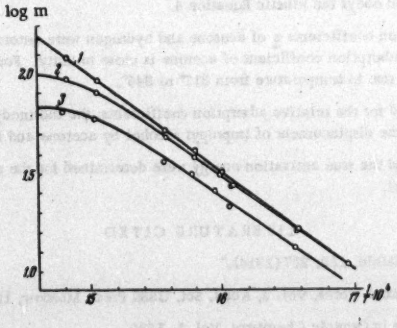

Fig. 10

the calculated activation energy. The values of the logarithm of the pre-exponential term which are given in Table 5 were calculated from the equation

$$\log k_0 = \frac{\epsilon}{4.57\,T} + \log k. \qquad (9)$$

The scatter of the values obtained is not great, so that Equation 5 is applicable. From the mean value of log k_0 we determined the value of the pre-exponential term $k_0 = 6.12 \cdot 10^8$ and the reciprocal of the scattering parameter $\epsilon/\log k_0 = 2.42 \cdot 10^3$. The true activation energy calculated from log $\underline{k}$ (ϵ = 23,650 cal/mole) differs from the activation energy calculated from log $\underline{m}$ (ϵ = 20,500 cal/mole), see Fig. 10, Curves 1 and 3. This indicates that the dehydrogenation of isopropyl alcohol is not a zero-order reaction, but proceeds according to Equation 4. The relative adsorption coefficient depends on temperature, and, in fact, increases with rise in temperature (Fig. 9). It can be seen that the relative adsorption coefficient of acetone is close to unity and changes little with temperature, whereas the relative adsorption coefficient of hydrogen is fairly close to zero and increases with rise in temperature. If log $\underline{z}$ is plotted as ordinate and 1/T as abscissa, then straight lines are obtained (Fig. 11).

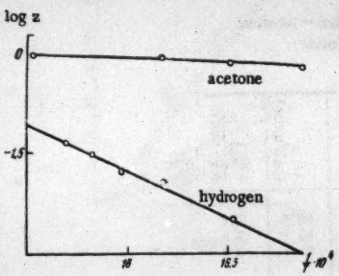

Fig. 11

At low temperatures the kinetic Equation 2 was found to be applicable; this does not contain adsorption coefficients. This can be seen from the fact that, if $\underline{k}$ is calculated from Equation 2 and log $\underline{k}$ is plotted against 1/T, the points lie on a straight line up to a point at which the temperature can no longer be considered low. At high temperatures the points fall below the straight line. Equation 2 is applicable because, in the given reaction at low temperatures z_a is approximately unity and z_s is approximately zero, i. e., just those conditions obtain for which Equation 2 was derived. At higher temperatures z_s increases and z_a, although still small, also increases; it is to be expected, therefore, that Equation 2 will no longer apply.

SUMMARY

1. A study was made of the kinetics of the dehydrogenation of isopropyl alcohol over manganous oxide. It was shown that this reaction obeys the kinetic Equation 4.

2. The relative adsorption coefficients $\underline{z}$ of acetone and hydrogen were determined. In the temperature range 330-400° the relative adsorption coefficient of acetone is close to unity. For hydrogen it varies from 0.10 to 0.36, increasing with rise in temperature from 317° to 345°.

3. From the values found for the relative adsorption coefficients, the thermodynamic quantities ΔF, ΔH and ΔS were determined for the displacement of isopropyl alcohol by acetone and hydrogen.

4. The rate constants and the true activation energy were determined for the dehydrogenation of isopropyl alcohol (ϵ = 23,650 cal/mole).

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BRIEF COMMUNICATIONS

COORDINATION NUMBERS OF Rb^+ AND Cs^+ IONS IN AQUEOUS SOLUTIONS

O. Ya. Samoilov

With the aid of a specially developed thermochemical method we have previously determined the coordination numbers of various ions, including Li^+, Na^+ and K^+ [1], in dilute aqueous solution. The present paper gives results of the determination of the coordination numbers of Rb^+ and Cs^+ ions. The integral heats of solution were measured for rubidium and cesium chlorides in water and in aqueous hydrochloric acid at 25°. An improved calorimeter having an isothermal jacket was used [2]. The temperature was read on a Beckmann thermometer, with the aid of a magnifier, accurately within 0.001°. The measurement of current strength and the introduction of the weighed sample were carried out as described previously [2]. The final RbCl and CsCl concentrations in the solution were 0.050 and 0.047 moles, respectively, of salt in 50 moles of water. The results of the measurements are given in the table. Heats of solution (L) are given in kcal/mole, and the HCl concentration (m) in moles of HCl per 50 moles of water. Individual measurements of L were accurate within about 1%.

TABLE

Integral Heats of Solution of RbCl and CsCl in Aqueous HCl Solutions at 25°

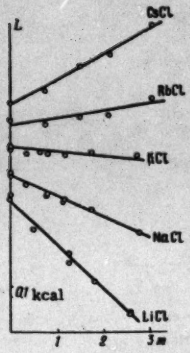
Dissolved salt	m	L	Dissolved salt	m	L
RbCl	0.00	−4.18	CsCl	0.00	−4.31
	0.72	−4.22		0.72	−4.17
	1.47	−4.14		1.47	−3.92
	2.08	−4.12		2.09	−3.80
	3.02	−3.95		3.03	−3.49

The relationships between L and m for RbCl and CsCl are shown in the figure together with the corresponding relationships for lithium, sodium, and potassium chlorides. In order to present these on one graph we have displaced the curves (straight lines) along the axis of ordinates while preserving contancy of scale.

The values of $\delta = -\Delta L/\Delta m$, determined by the method of least squares, are −85 and −274 for RbCl and CsCl respectively. The values of the coordination numbers of Rb^+ and Cs^+ may be found from the relation [1]

$$1.17 \cdot 10^3 \left(\frac{n}{r + 1.38} - \frac{4.4}{3.19} \right) = \beta,$$

in which n is the coordination number of the cation and r is its crystallographic radius; the coordination number and radius of the Cl^- ion are taken to be 4.4 and 1.81 A respectively [1]. Using the Goldschmidt radii of the Rb^+ and Cs^+ ions (1.49 and 1.65 A), we find that $n_{Rb^+} = 3.8$ and $n_{Cs^+} = 3.5$. The values of $\rho^{\frac{1}{3}}$ [1] for Rb^+ and Cs^+ are 0.037 and 0.030 A^{-1} respectively. These cations are characterized by negative hydration (for Cs^+



Dependence of integral heats of solution of alkali-metal chlorides (L) on the concentration of HCl in the solvent (m).

$\Delta E = -0.33$ kcal/mole [3]). This fact is probably of great importance for the behavior of Rb^+ and Cs^+ in the natural aqueous solutions of the earth's crust. In particular, it is significant that the temperature coefficient of the mobility of ions that have negative hydration is less than that of water molecules [4].

SUMMARY

1. The coordination numbers of the cations Rb^+ and Cs^+ were determined in dilute aqueous solutions by the thermochemical method and found to be 3.8 and 3.5, respectively.

2. The Rb^+ and Cs^+ cations are characterized by negative hydration.

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HEAT OF ATOMIZATION OF CARBON

G.V. Bykov

In the course of establishing the relationship between electronic charges of bonds and heats of formation of saturated hydrocarbons the author [1] found that the energies of the C–C and C–H bonds formed by two σ-electrons are 16.108 and 64.616 kcal/mole respectively, and the heat of atomization of carbon is 32.216 kcal/g-atom. As the heat of sublimation of diamond probably lies between 124 kcal (lower limit) and 170 kcal (upper limit) and the values calculated on this basis for the energy of the C–H bond in methane are 87.6 and 91.1 kcal respectively, the values obtained by the author require some further substantiation.

According to Cottrell's data ([2], pp. 226-227), the bond energies in HF, H_2O and NH_3 are $D_{HF} = 135$, $D_{OH} = 110.6$ and $D_{NH} = 84.3$ kcal. According to the position of carbon in the periodic system, the energy of the C–H bond in CH_4 should be still less. We may attempt to evaluate this bond energy on the assumption that the difference $D_{NH} - D_{CH}$ is similar to $D_{HF} - D_{OH} = 24.4$ and $D_{OH} - D_{NH} = 26.3$ kcal. D_{CH} should then be about 59 kcal, to which our figure is the closest.

Some theoretical chemists, and particularly Long [3, 4], have developed the idea that bond energies calculated in the usual way cannot be correlated with interatomic distances, force constants, and other bond characteristics, and that such correlation is possible only for "true" ("natural", "absolute," or "intrinsic") bond energies. We obtain the latter if in our calculations we take not the heat of atomization of carbon into atoms in their "fundamental" state, but the heat of an atomization process in which the atoms obtained preserve the valence state that they had in the molecules. As neither the energy of the valence state nor true bond energies can be determined directly, attempts were made to evaluate them by indirect methods, but no reliable results were obtained. The author considers that the value he has found of about 30 kcal/g-atom is the required heat of atomization of carbon to atoms in their valence state, and we shall term this the valence heat of atomization of carbon and denote it by L_{C_v}.

Let us consider the usual thermochemical scheme used in the calculation of the heat of formation (atomization) of a gaseous hydrocarbon C_nH_m.

$$C_nH_m(g) + \left(n + \frac{m}{4}\right)O_2(g) = nCO_2(g) + \frac{m}{2}H_2O(l) + \Delta H^0_{C_nH_m}\ (\text{combust}) \qquad (1)$$

$$nC(s) + nO_2(g) = nCO_2(g) + n\Delta H^0_{CO_2} \qquad (2)$$

$$\frac{m}{2}H_2(g) + \frac{m}{4}O_2(g) = \frac{m}{2}H_2O(l) + \frac{m}{2}\Delta H^0_{H_2O}. \qquad (3)$$

Subtracting (1) from the sum of (2) and (3), we obtain

$$nC(s) + \frac{m}{2}H_2(g) = C_nH_m(g) + \Delta H^0_{C_nH_m}\ (el), \qquad (4)$$

in which the heat of formation of the hydrocarbon C_nH_m from its elements is

$$\Delta H^0_{C_nH_m}(\text{el}) = n\Delta H^0_{CO_2} + \frac{m}{2}\Delta H^0_{H_2O} - \Delta H^0_{C_nH_m}(\text{combust}) \quad (5)$$

For the calculation of the heat of formation of the hydrocarbon C_nH_m from its atoms we require two more equations:

$$nC(s) = nC(g) + n\Delta H^0_C; \quad (6)$$

$$\frac{m}{2}H_2(g) = mH(g) + \frac{m}{2}\Delta H^0_{H_2}. \quad (7)$$

Subtracting (6) and (7) from (4), we obtain

$$nC(g) + mH(g) = C_nH_m(g) + \Delta H^0_{C_nH_m}(\text{at}), \quad (8)$$

in which

$$\Delta H^0_{C_nH_m}(\text{at}) = \Delta H^0_{C_nH_m}(\text{el}) - \frac{m}{2}\Delta H^0_{H_2} - n\Delta H^0_C \quad (9)$$

or in accordance with (5)

$$\Delta H^0_{C_nH_m}(\text{at}) = n\Delta H^0_{CO_2} + \frac{m}{2}\Delta H^0_{H_2O} - \Delta H^0_{C_nH_m}(\text{combust}) - \frac{m}{2}\Delta H^0_{H_2} - n\Delta H^0_C \quad (10)$$

The first four terms of the right-hand side of this equation are experimentally determinable quantities and cannot give rise to doubt. However, the true value of the so-called heat of sublimation of diamond ΔH^0_C is unknown and, what is more important, the substitution of a value for this in Equation 6 is not permissible if we are proposing to calculate true bond energies.

Actually, the processes represented by Equations 1, 2 and 4 consist in the passage of carbon from one compound to another with preservation of its valence state.* Similarly, in Equation 8 carbon C (g) passes into the valence state. Hence, in Equation 6 also, contrary to usual practice, we must introduce C (g) in the fundamental state and identify ΔH^0_C with the heat of sublimation of diamond in this equation and also in Equations 9 and 10. If we could in some way solve Equation 9 or 10 numerically for ΔH^0_C, we should obtain not the heat of sublimation of diamond, but the valence heat of atomization of carbon. As the author has shown [1], this can be done in the case of saturated hydrocarbons by use of the relationship

$$-\Delta H^0_{C_nH_{2n+2}}(\text{at}) = a\Sigma A^v_{CC} + b\Sigma A^v_{CH}, \quad (11)$$

* We neglect the differences in the valence states of carbon in CO_2, diamond, graphite, and hydrocarbons in the present case, although it would be necessary to take them into account in more precise calculations.

in which ΣA^{σ}_{CC} and ΣA^{σ}_{CH} are summated σ-electron charges of C–C and C–H bonds, respectively, calculated from the equation proposed by the author; $\underline{a} = \frac{1}{4} L_{C_V}$; and $\underline{b}$ can be readily expressed in an explicit form in terms of $\underline{a}$.

In Long's opinion, the energy of the valence state of the carbon atom is higher (approximately by 60–70 kcal) than the energy of the fundamental state, and the true bond energies are higher than those calculated in accordance with the usual scheme. However, we do not really know anything definite about the valence states of carbon (see [2], p.104 et seq.); every such statement must have a hypothetical character. Evidence against Long's view is found in the fact that, in accordance with the high energy of the valence state, atomic carbon gas–being, it is thought, in the fundamental state– should be fairly stable, which is not in accord with experiment. The facts can be given another explanation: the quadrivalent state of carbon is energetically the most favorable and any transition from this state to any other is accompanied by absorption of energy. For example, according to the author's estimation, 35 kcal is required for the conversion of one g-atom of carbon from the quadrivalent state (in methane) into the tervalent state (in the methyl radical). This is to be explained by the fact that the dissociation energy of the C–H bond in methane, and particularly of the C–C bond in ethane, is considerably greater than the true bond energy.

SUMMARY

1. The energy of the C–H bond in methane is about 64 kcal and is in accord with the position of carbon in the periodic system.

2. The heat of atomization of carbon into atoms that preserve their valence state is approximately 32 kcal/g-atom.

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SYNTHESIS OF CANCEROLYTIC PEPTIDES

I. L. Knunyants, O. V. Kildisheva and N. E. Golubeva

By reaction of the N-formyl derivative of 3-p-(bis-2-chloroethylamino)-phenylalanine ("Sarcolysine") with various amino-acid esters we obtained a series of previously unknown peptides containing the bis-2-chloroethylamino group (see table). For the condensation we made use of dicyclohexylcarbodiimide, previously proposed by Sheehan for the preparation of simple peptides [1].

EXPERIMENTAL

Previously purified DL-3-p-(bis-2-chloroethylamino) phenylalanine [2], m.p. 179-180° with decomposition, was heated in a mixture of anhydrous formic acid and acetic anhydride (3:1) in a water bath at 45-50° for 45 minutes. The resulting DL-3-p-(bis-2-chloroethylamino) phenyl-N-formylalanine was isolated by diluting the cooled solution with water. It formed colorless needles from methanol, m.p. 148-150°. Yield 65-70%.

Found %: C 50.24; H 5.51; N 8.45 $C_{14}H_{18}N_2Cl_2O_3$. Calculated %: C 50.46; H 5.44; N 8.47

Successive additions were made of equimolecular amounts of dicyclohexylcarbodiimide and the appropriate racemic amino-acid ester in chloroform to a suspension of 1 mole of DL-3-p-(bis-2-chloroethylamino) phenyl-N-formylalanine in chloroform. The mixture was shaken vigorously and then left at room temperature for 5-6 hours. The precipitated 1,3-dicyclohexylurea was filtered off, chloroform was distilled from the filtrate, and the residue was mixed with a little alcohol and allowed to crystallize in a refrigerator. The precipitated dipeptide was filtered off and recrystallized from alcohol (see table). By this general method we prepared the ethyl esters of (N-formylsarcolysyl) phenylalanine, (N-formylsarcolysyl)-β-alanine, (N-formylsarcolysyl) valine, and (N-formylsarcolysyl) leucine, and also the methyl ester of (N-formylsarcolysyl) tryptophan. The properties of these peptides are shown in the table.

SUMMARY

New peptides containing a bis-2-chloroethylamino group were prepared by condensing DL-3-p-(bis-2-chloroethylamino) phenyl-N-formylalanine with amino-acid esters.

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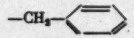
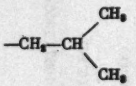
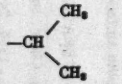
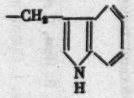
Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR

TABLE

R	R′	Found (%)				Calculated (%)				M. p. (°C)	Recrystallized from	Yield (%)
		C	H	N	Cl	C	H	N	Cl			
$-COOC_2H_5$		59.02	6.23	8.44	13.50	59.05	6.14	8.26	13.95	116—120	Ethanol	73
$-COOC_2H_5$		55.72	7.12	8.73	—	55.69	7.22	8.85	—	114—117	Ethanol	40
$-CH_2COOC_2H_5$	H	—	—	9.57	16.61	—	—	9.72	16.43	138—140	Ethanol	57
$-COOC_2H_5$		54.99	6.96	8.78	15.42	54.78	6.78	9.12	15.40	130—132	Ethanol	69
$-COOCH_3$		58.20	5.89	—	13.83	58.54	5.67	—	13.29	151—152	Methanol	47

CIS–TRANS ISOMERISM OF 1,2-BISTRICHLOROSILYLETHYLENE

M. I Batuev, V. A. Ponomarenko, A. D. Matveeva

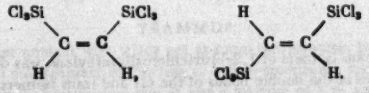
and A. D. Snegova

1,2-Bistrichlorosilylethylene [1,1,1,4,4,4-hexachloro-1,4-disilabut-2-ene] was prepared by dehydrochlorination of $Cl_3SiCH(Cl)CH_2SiCl_3$ with the aid of quinoline. Under these conditions formation of unsymmetrically substituted ethylenes is not observed.* The boiling point of $Cl_3Si-CH=CH-SiCl_3$ is 192-192.5° (744.5 mm) and its melting point is about 36°. The Raman spectrum of this substance was determined on a Soviet ISP-51 three-prism spectrograph with a central camera; the exciting radiation was the 4358 A line from a mercury lamp.

$\Delta\nu$ cm^{-1}: 97 (1), 115 (1), 129 (6), 153 (5*), 171 (4*), 194 (4), 301 (1*), 316 (9*), 351 (0), 464 (0), 483 (1*), 498 (9*), 581 (3*), —591 (3*) —807 (3*), (band), 620 (0), 743 (1), 757 (0), 774 (0), 1282 (6*), 1297 (6*), 1559 (5), 1602 (5), 2889 (1), 2957 (5 d)

d Denotes doublet, and the asterisks indicate lines occurring on a general background.

The presence in the spectrum of distinct and widely spaced lines in the double bond region having identical intensities—1559 (5) and 1602 (5)— definitely indicates that the substance investigated is a mixture of two isomers, cis and trans, present in approximately equal amounts:



This explains the comparatively large number of lines in the spectrum for a symmetrical compound of this type and the presence of closely placed or double (nor sharply split into two) lines (1282 and 1297, 2975 (d)); the two lines of each of these pairs belong to different isomers. The effect of the chlorine atoms of the trichlorosilyl groups is manifested by a somewhat low level of frequencies of the double bond for both isomers.

* The unsymmetrical derivative $(SiCl_3)_2C=CH_2$ was obtained [1], together with the symmetrical derivative $Cl_3Si-CH=CH-SiCl_3$ from $Cl_3Si-CH(Cl)CH_2-SiCl_3$ by dehydrochlorination with the aid of $AlCl_3$. The resolution of the products of the methylation of $Cl_3Si-CH=CH-SiCl_3$ into cis and trans isomers was not carried out either chemically or spectrographically in the investigation [1].

As fairly extensive experimental data show, in cis isomers the vibrational frequency of the double bond is generally somewhat lower than in the corresponding trans isomers [2], e.g., (cm^{-1}):

$H_3C-CH=CH-CH_3$	cis	1669
	trans	1681
$H_3C(CH_2)_n-CH=CH-CH_3$	cis	1658
	trans	1674
$H_3C(CH_2)_3-CH=CH-(CH_2)_3CH_3$	cis	1653
	trans	1667
$H_3C-CH=CH-CO\cdot OCH_3$	cis	1644
	trans	1655
$H_5C_6-CH=CH-C_6H_5$	cis	1640
	trans	1652

A similar relation of frequencies is evidently found in the isomers under consideration (cm^{-1}):

$Cl_3Si-CH=CH-SiCl_3$	cis	1559
	trans	1602

but in this case the difference in frequency of the double bond in the two isomers (43 cm^{-1}) is substantially greater than for the cis and trans isomers cited above for comparison (11-16 cm^{-1}).

Owing to the almost identical boiling points of these isomers, we did not succeed in separating them chemically (by fractionation).

It may be noted that in [1] the authors found a very broad line (breadth about 20 cm^{-1}) in the spectrum of $(CH_3)_3Si-CH=CH-Si(CH_3)_3$ in the double-bond region. They did not associate it with the presence of cis and trans isomers in the substance under investigation. In the light of our results there can be no doubt that in [1] the authors were dealing with a mixture of the cis and trans isomers of $(CH_3)_3Si-CH=CH-Si(CH_3)_3$, which are characterized by different frequencies in the double-bond region, these, however, being not so far apart as in the cis and trans isomers of $Cl_3Si-CH=CH-SiCl_3$ so that in the experiment of the authors of [1] they were merged into one broad line.

SUMMARY

The existence of cis and trans isomers of 1,2-bistrichlorosilylethylene was detected spectrographically. It was noted that the frequencies of the double bonds of the cis and trans isomers of 1,2-bistrichlorosilyethylene are unusually far apart as compared with the frequencies found for the cis and trans isomers of other compounds.

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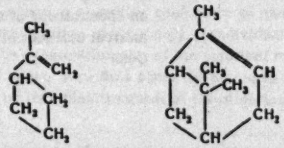
ISOMERIZATION OF ISOPROPENYLCYCLOBUTANE ON SILICA GEL UNDER THE CONDITIONS OF CHROMATOGRAPHIC ADSORPTIONAL ANALYSIS

B. A. Kazansky, M. Yu. Lukina, L. A. Nakhapetyan
V. T. Aleksanyan and Kh. E. Sterin

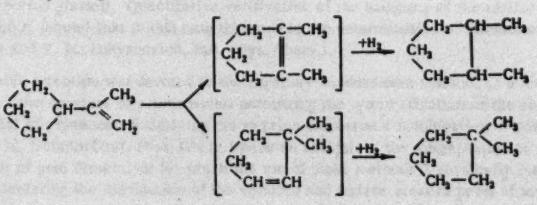
We have previously observed that alkylcyclobutanes [1], unlike alkylcyclopropanes [2], do not isomerize in contact with silica gel under the conditions of chromatographic adsorptional analysis. It was, therefore, somewhat unexpected that pinene, which contains a four-membered ring, should be found [3] to be isomerized into a mixture of camphene, dipentene and terpinolene when attempts were made to purify it by chromatographic adsorption on silica gel.

As isopropenylcyclobutane was available to us, we decided to investigate its behavior toward silica gel, for its structure is reminiscent of the part of the pinene molecule that participates in the isomerization.



Our experiments showed that, after contact with silica gel at room temperature, isopropenylcyclobutane had been isomerized completely with enlargement of the ring to a five-membered system. The Raman spectrum of the hydrogenated isomerization product showed that it was a mixture of 1,2- and 1,1-dimethylcyclopentanes.

The reaction may be represented as follows:



EXPERIMENTAL

Isopropenylcyclobutane (7.8 g; b.p. 98.7° n_D^{20} 1.4347; d_4^{20} 0.7743) was filtered through a column containing 128 g of silica gel (Quality KSM (a) 12.0). The product distilled at 100-105° (760 mm) and had n_D^{20} 1.4426; d^{20} 0.7918. The isomerization product was hydrogenated in alcoholic solution at room temperature over platinized charcoal in a hydrogenation flask. The resulting hydrocarbon was steam-distilled, and the hydrocarbon layer was washed free of traces of alcohol with water, dried over calcium chloride, and distilled. The yield of hydrocarbon was 5.8 g; b.p. 92-97°; n_D^{20} 1.4152; d_4^{20} 0.7578.

Investigation of the Raman spectrum of this hydrocarbon showed that it was a mixture of 70% of trans-1, 2-dimethylcyclopentane (262, 398, 529, 607, 766, 897, 955 and 1080 cm^{-1}), 15% of cis-1,2-dimethylcyclopentane (498, 766 and 889 cm^{-1}), and 15% of 1,1-dimethylcyclopentane (562 cm^{-1}).

SUMMARY

It was shown that, under the conditions of chromatographic adsorptional analysis on silica gel, isopropenylcyclobutane is isomerized with enlargement of the ring.

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CURRENT EVENTS

SECOND CONFERENCE ON METHODS OF INVESTIGATING THE STRUCTURE OF HIGHLY DISPERSED AND AND POROUS BODIES

The second conference on methods of investigating the structure of highly dispersed and porous bodies, organized by the Institutes of Physical Chemistry and of Silicate Chemistry of the Academy of Sciences of the USSR, took place on June 13-18, 1956, at the Institute of Silicate Chemistry in Leningrad (the first conference took place in 1951). Representatives of other Academy and branch institutes interested in this subject took part in the work of the conference.

Such conferences are very valuable because of the wide use of sorbents and catalysts in industry and of the great practical importance of thenature of their porosity. As a result of the first conference, plans were made for interrelated investigations on the structure of porous bodies with the aid of various methods, so that these methods could be checked against one another and the limits of applicability of each method could be more precisely defined. The second conference showed that the projected program had been substantially completed thanks to the joint investigations carried out by various institutes.

The second conference was planned as a working conference of narrow scope and of a methodological character. It was devoted to an examination of the theory of individual methods of investigating the structure of highly dispersed bodies and to an examination also of the practical results achieved in the development of these methods during the last five years. New data about the porous structure of various bodies were examined as illustrations of the possibilities of individual methods of investigation. In all, twenty papers were read, and they prompted a lively discussion.

First of all, an examination was made of methods based on the small-angle scattering of x-rays and on the use of the electron microscope. E. A. Porai-Koshits (Inst. Silicate Chem.) reported on new possibilities of extending the limits of application of the method of small-angle scattering of x-rays: the use of recently developed apparatus makes it possible, for example, to make an approach to the determination of regions of heterogeniety corresponding in dimensions to formations made up of only a few atoms. Use of the replica method in electron-microscopy has made it possible to show very clearly that porous bodies fall into two groups: 1) those of globular structure (silica gels, aluminosilicate catalysts, titania gels, etc.), and 2) those of spongy structure (active charcoals and porous glasses). Quantitative verification of the accuracy of the replica method for particles of the order of 100 A showed that in this case the error in the determination of dimensions is of the order of 10% (E. A. Lentyev and V. M. Lukyanovich, Inst. Phys. Chem.).

Considerable attention was devoted to the capillary condensation method, as a fundamental method in the investigation of the structure of porous bodies permitting the systematization of the enormous amount of experimental material in existence. Examining the sorption process as a combination of adsorption and capillary condensation, M. M. Dubinin (Inst. Phys. Chem.) gave an analysis of the assumptions and made an evaluation of the lower limit of pore dimensions for which the use of these methods is physically justified. He then examined methods of calculating the distribution of the volumes and surface areas of pores of sorbents with respect to their dimensions and methods of introducing corrections for the thicknesses and volumes of adsorption layers; he also made an appraisal of simplified methods of calculation.

The process of capillary condensation of vapor in bodies of globular structure was subjected to detailed analysis. A. V. Kiselev (Inst. Chem. Physics and Moscow State University) raised the general questions of the

structure of adsorbents in its relation to their formation. He stated various facts that enable us to assign a corpuscular – in particular, globular – structure to the skeleton of many gel adsorbents. In such structures the primary particles probably preserve their individuality; their dimensions determine the specific surface of the sorbent and the pores are the spaces between the particles. The other extreme case is that of spongy structures, which are formed by the attack of corrosive gases or solutions on solids. L. V. Radushkevich (Inst. Phys. Chem.) gave a rigorous calculation of the isotherms of reversible capillary condensation for a model adsorbent formed by spherical particles in contact. Close agreement of these theoretical calculations with experiment was found for a sample of compressed carbon black made up of nonporous particles of diameter greater than 1000 A, as measured under the electron microscope. In the development of these ideas, A. P. Karnaukhov (Moscow State University) expounded the theory of capillary-condensation hysteresis in regularly packed globular structures considered as a function of the coordination number. As was pointed out in the discussion, the above-mentioned papers enable us to understand the peculiar features of the capillary-condensation process in model systems and, in the future, we must try to estimate the extent to which the usual sorbents of globular structure approach these models.

S. P. Zhdanov (Inst. Silicate Chem.), taking porous glasses as his examples, pointed out some peculiarities of sorption processes in bodies of spongy structure. D. P. Dobychin (State Optical Inst.) demonstrated the power of the capillary-condensation method in the determination of the changes in the structure of porous glasses under the action of thermal treatment. V. S. Nabokov, E. N. Paleolog and N. D. Tomashov (Inst. Phys. Chem.) reported the successful application of the capillary-condensation method in the study of the porosity of films on anodized aluminum. The general laws determining change in sorption properties and form of isotherm were found for fluorinated (I. E. Neimark, Inst. Phys. Chem.) and chlorinated (K. D. Shcherbakova, Moscow State University) silica gels. The effects due to modification of the chemical nature of the sorbent surface are of great theoretical and practical interest and require further investigation, as was pointed out in the discussion. Simplified methods of calculation in the analysis of the porous structure of natural sorbents were analyzed by G. V. Tsitsishvili (Inst. Chem. Acad. Sci. Georgian SSR).

After an examination of the possibilities of these methods, a separate session was devoted to a comparison of the results obtained by independent methods of investigation. A study of the structures of various silica gels, aluminosilicate catalysts, and carbon sorbents by electron-microscope methods and by the method of small-angle scattering of x-rays (A. V. Kisel, V. M. Lukyanovich and E. A. Porai-Koshits) showed that, in the main, there was agreement between the results of different methods as regards the sizes of the particles making up these bodies. Apart from mutual confirmation, these data made it possible to obtain a more complete picture of the structure of certain bodies, particularly aluminosilicate catalysts. Nevertheless, in certain cases discrepancies appeared which demanded further investigation. The combined use of the method of small-angle scattering of x-rays and the method of capillary condensation for bodies of spongy structure was demonstrated by E. A. Porai-Koshits and S. P. Zhdanov for the case of porous glasses of variable structure.

Another separate session was devoted to some methods of determining the specific surfaces of highly dispersed systems. The adsorption method was not considered, because it was analyzed in detail at the 1951 conference. B. V. Deryagin, N. N. Zakhavaeva, M. V. Talaev and V. V. Filippovsky (Inst. Phys. Chem.) considered filtration methods of determining the specific surfaces of powders and porous bodies. These methods are simple in operation, and in some cases they are sufficiently accurate. By a combination of measurements made by methods of stationary and nonstationary streams, indications may be obtained of the presence and extent of pores in the particles. A. M. Smirnova, N. G. Zaitseva and V. P. Sukhova (Inst. Phys. Chem.) reported the application of the labeled-atom method to the measurement of the specific surface of cements in the hydration process. The method makes it possible to follow the changes in the specific surface of solids in an aqueous medium, although it is often difficult to distinguish between surface exchange and exchange that goes deep into the crystal lattice. A promising simple dynamic method of determining the structures and specific surfaces of adsorbents was described by V. T. Bykov and O. E. Presnyakova (Far-East Affiliated Inst. of Acad. Sci. USSR). By using substances having molecules of different sizes and analyzing the form of the efflux curves, the authors were able to draw conclusions regarding the structures of several natural adsorbents and regarding the rate of the adsorption process. The method of adsorption chemistry was discussed in a paper by S. Yu. Elovich and L. Ya. Margolis (Inst. Phys. Chem.): investigating the chemisorption of carbon monoxide on manganese dioxide, the authors were able to estimate the surface of individual elements of the lattice, in particular oxygen, and so break down the general surface of the body into its elements.

Papers by T. G. Plachenov and G. M. Belotserkovsky (Leningrad Technological Inst.) dealt with the use of the method of forcing mercury into the sorbent for analyzing its porous structure. In the discussion on this question it was pointed out that the fact that different amounts of mercury remained in different samples after removal of pressure opened up new possibilities for the understanding of the porous structure of sorbents— investigations in this direction must be extended. By the introduction of improvements in the method, S. A. Semenova succeeded in extending the range of applicability of the method in the direction of low pressures and carrying out reliable measurements of the volume of the large macropores in active carbons. The method of mercury porometry was used for measuring large pores in natural sorbents and showed the difference in porous structure between genetically differing groups of these sorbents—diatomites, tuffs, etc., (N. I. Zalevsky and V. T. Bykov, Far-East Polytechnical Institute).

In the discussions that followed papers on allied and border-line topics, considerable attention was devoted to the principles underlying the methods and to an analysis of the assumptions made. These topics are closely associated with the problem of the interpretation of experimental results, the solution of which is often difficult owing to the great variety of porous structures and the frequent complexity of their character. The capillary-condensation method, for example, is based on the derivation of the distribution of pore volume with respect to pore size from the desorption branch of the isotherm, i.e., the complex structure of the real porous body is represented as that of some equivalent sorbent, which, in the simplest case, may be a collection of capillaries of different diameters. The validity of this representation is the greater, the more closely the form of the pores of the real sorbent approximates to cylindrical or to that assumed in the equivalent model sorbent. However, as V. V. Serpinsky (Inst. Phys. Chem.) pointed out, the characterization of a porous structure with the aid of a distribution with respect to a linear parameter is not the only one possible and may not be the best method. It is possible to characterize the porosity of a sorbent on the basis of adsorption isotherms in a way satisfying practical requirements without introducing the concept of pores having a fictitious cylindrical form of definite radius. On the other hand, as was pointed out in the discussion, the existing method has the advantage of presenting a lucid picture of the phenomenon and enabling us to systematize extensive experimental material.

An urgent general problem in all the methods is the establishment of physically well-grounded limits of applicability. For the capillary-condensation method the whole matter rests on the determination of the lowest pore diameter in which a liquid meniscus is formed. In the method of mercury porometry the increase in pressure must not be too great owing to deformation of sorbent and for other reasons. In electron microscopy the exact limits of resolution attainable in the replica method have not been determined, and so on. This matter was analyzed in the discussion for these and other methods. One of the most important methods of solving this problem, and also the problem of the interpretation of experimental results, is the method of joint coordinated investigations of model samples of porous bodies by the use of various methods.

Many of the various methods of investigating the structure of porous and highly dispersed bodies are associated with a great variety of practical problems. Each method has its advantages and limitations, and all methods must be developed. Some of these methods are widely used in industry, and in the future it is necessary, on the one hand, to carry out work on the standardization of simplified methods for direct application in practice and, on the other to push on with the development of other promising methods.

In the resolution carried at the conference it is noted that the conference has carried out fruitful work. A critical analysis was made of the premises lying at the basis of various methods, the practical achievements of the last five years were examined, and plans were laid for the further development of joint investigations on the structure of highly dispersed and porous bodies by the various available methods. An important condition for the successful performance of joint investigations is the preparation of series of standard sorbents in which structural characteristics are varied in a regular manner. Industry provides very few standardized adsorbents, and these cannot meet practical requirements for the purposes of recuperation, chromatographic separation of mixtures, etc. The conference, therefore, asked the Division of Chemical Sciences of the Academy of Sciences of the USSR to request the Ministry of Chemical Industry to organize the manufacture of series of standardized adsorbents in which structural characteristics are varied in a regular manner (in the first place, silica gels and active carbons).

The conference plans to distribute work on the preparation of standard adsorbents and the development of individual methods of investigating the structure of highly dispersed and porous bodies over several laboratories. It is essential to aim at the greatest possible development of conjoint investigations, and the main problem must

be the analysis and correlation of the structural characteristics, as found by the aid of different methods.

The conference noted the importance of studying the processes by which a porous structure is formed in a body. Investigation of these processes is bound to aid in the development of more profound concepts of the structure of porous systems, particularly with respect to their assignment to the globular or spongy type (new possibilities in this direction are provided by the elegant method described by N. M. Kamakin (Grozny Petroleum Researach Institute) in which gels are "frozen" and the dispersion medium is sublimed; this makes it possible to follow changes in structure in the transition from hydrogels to xerogels).

The conference elected a committee under the chairmanship of M. M. Dubinin for the coordination of conjoint investigations and the organization of the preparation and exchange of standard samples. The conference commissioned the committee to approach the directorates of various institutes with requests for cooperation in the development of individual methods of investigating the structure of porous bodies and for the inclusion of appropriate investigations in the plans of the institutes.

The work of the conference will be published in the form of a collection of transactions.

In conclusion we must remark on the excellent organization of the conference: the sessions began on time, the lecturers kept strictly to the regulations, and, as the time allowed for the papers was 20-30 minutes, there remained adequate time for discussion.

V. M. Lukyanovich

CONGRESS OF AUSTRIAN AND GERMAN CHEMISTS

A congress of Austrian and German chemists was held at the end of April 1956 at Salzburg, Austria. Two Soviet scientists took part: N. N. Vorozhtsov, Doctor of Chemical Sciences, Professor of the D. I. Mendeleev Institute of Chemistry and Technology, Moscow, and M. A. Klochko, Doctor of the Chemical Sciences, Director of the Laboratory of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR. The work of the congress occupied three days, April 26-28. The first two days were devoted to scientific papers, and the third to excursions to various institutes and other undertakings and to tours of the city of Salzburg.

The congress was opened on the morning of April 26. After addresses of welcome from representatives of the Austrian Ministry of Education, the City Council, and other organizations, the plenary session was held. At this session two papers were read, and work then continued for the rest of the day — with a break for dinner — in two sessions: organic chemistry and inorganic and physical chemistry. Most of the participants were from Austria, the German Federal Republic and the German Democratic Republic. Chemists also came from Britain, Belgium, Switzerland, the USA, Italy, and other countries. In all, more than five hundred people took part in the congress. Papers were read by chemists from Austria, the German Federal Republic and the German Democratic Republic. Respresentatives from the USA and Holland gave one paper each; one paper was in the names of Austrian and Swedish chemists, and one was in the names of Austrian and Egyptian investigators.

The first paper of the morning session of April 26 was by Professor L. Audrieth of Illinois University (Urbana, Ill.); it was entitled "Recent Progress in the Chemistry of Hydrazine." Professor Audrieth has carried out many fruitful investigations on the chemistry of hydrazine and its derivatives, which he has made into a orderly system. His paper described this work. The second paper, "Intermediate Compounds in Chemical Reactions With Solids," was given by Professor G. F. Huttig of the Technical High School in Graz (Austria). Professor Huttig is a specialist on reactions in the solid state and has published many experimental and theoretical papers on interaction between solids and on the catalytic properties of solids (which depends not only on composition, but also on the method of preparing the catalysts). He has recently turned his attention to grinding processes regarded from the chemical viewpoint. Professor Huttig discussed investigations on phase transitions in the solid

state at different temperatures and the associated changes in various properties of the system.

At the plenary session of April 27, papers were read by Professor R. Huisgen of Munich University on "Recent Results on the Chemistry of Medium-Sized Rings" and by Professor K. G. Peters of Vienna Technical High School on "New Methods of Separating Chemically Related Elements." Professor Peters described some interesting results obtained in the study of compounds formed by various metals with oxalic acid and its salts. For example, by the use of aluminum oxalate Peters has succeeded in separating rare earths.

At the section devoted to inorganic and physical chemistry on April 26 and 27, papers were read and discussed on inorganic, analytical and physical chemistry, and also on geochemistry. Abstracts of the papers had been published beforehand in a special issue of Osterreichische Chemiker Zeitung (57, 9/10, 1956), which was distributed to participants of the congress. Among papers on inorganic chemistry, great interest was aroused by a communication from P. Ehrlich (Chemical Institute of the J. Liebig High School, Giessen, German Federal Republic) on hydride-halides of alkaline-earth metals. These compounds were prepared by fusing the hydride and anhydrous halide together, or by fusing themetal with the halide in a hydrogen atmosphere. The author has studied the physical and chemical properties of these compounds.

A. Meuwsen and H. Tischler (Institute of Inorganic Chemistry, Erlangen University, German Federal Republic) discussed methods of preparing hydrazinesulfonates.

M. Baudler and L. Schmidt (Chemical Institute, Cologne University) reported on new methods for preparing pure P_2H_4, a substance that is extremely light-sensitive and unstable. The Raman spectrum of this substance and its reactions with various compounds were studied. At this section a paper was read also by G. Fritz and W. Raabe (Institute of Silicon Chemistry, Marburg University) on the "Preparation of Cyclic Sila-hydrocarbons by the Thermal Decomposition of $Si(CH_3)_4$." Among the products formed was a compound with a six-membered ring in which CH_2 and $Si(CH_3)_2$ groups alternated.

Another paper which might be described equally as inorganic or organic chemistry was on the subject "Acetylenic Derivatives of Boron" and was given by U. Kruerke of the Institute of Inorganic Chemistry, Munich University. These substances, which have the formula $\equiv B-C\equiv C-R$ and are called ethynylboron compounds, are closer in properties to etherates of boron ($\equiv B-O-C\equiv$) than to alkylborons ($\equiv B-C-C\equiv$).

A group of papers was devoted to analytical chemistry and geochemistry. H. Baliczo and H. Schiffner of Vienna University reported on a new gravimetric method of determining fluorine by precipitation with a solution of triphenyltin chloride in chloroform. The precipitate formed at the interface between the two phases (aqueous and chloroform) is free from excess of precipitant and from salt contaminants which may be present in the solution under investigation. There were two communications on geochemistry. The first, which was by E. Broda, K. Nowotny, T. Schonfeld and O. Suschny (Chemical Laboratory, Vienna University) was devoted to the determination of the uranium content of the ash of Austrian brown coals. Eighteen samples were analyzed by the radiochemical method, and 8-100 g of uranium per metric ton of ash was found. The second discussed the investigation of the uranium contents of sea-bed deposits in the Baltic Sea. The authors -- F. Hecht, F. Kotzy (Goteborg, Sweden), R. Patzak and E. Tomic (Vienna University) -- associate the uranium content of samples with the closeness of the sampling point to estuaries of rivers that flow across various rocks. Sedimentary rocks are more enriched in uranium than primary rocks, and this affects the composition of river water. Uranium compounds are precipitated in the colloidal state and are carried out to sea, where they join the sea-bed deposits.

A series of papers was devoted to various branches of physical chemistry -- problems relating to the chemical bond, molecular structure, kinetics, etc. E. Harter and O. Glemser (Gottingen University) reported on the determination of the distance between metal and oxygen in hydroxides, basic salts, and hydrates by the optical method.

W. Bues (Technical High School, Stuttgart) has investigated the structure of polyphosphate melts. In his paper he pointed out that results obtained by the study of Raman and infrared spectra indicate partial preservation of the orderly arrangement peculiar to a crystalline structure even in the liquid state somewhat above the melting point. K. H. Lieser (Technical High School, Darmstadt) reported a study of the temperature-dependence of various properties of silver iodide (specific heat, coefficient of thermal expansion, electrical conductivity) with the object of obtaining data on the degree of order in various modifications of this substance.

Among papers on the kinetics of chemical processes was one by H. Schmid and E. Hallaba (Institute of Physical Chemistry, Technical High School, Vienna and Alexandria University, Egypt) on the "Kinetics and Mechanism of the Diazotization of Chloroaniline in Hydrochloric Acid Solution." H. Han and F. Burou (Kiel University) described the determination of the enthalpy of formation of gallium and indium sulfides, selenides, and tellurides by combustion in oxygen of the compounds and also mixtures of the two elements in a microcalorimetric bomb. For each metal, the enthalpy falls from the sulfide to the telluride.

In the Organic Chemistry Section, of 25 papers 14 were devoted to the synthesis of various substances and 11 to biochemistry. Among the first group was a paper by R. Koster (Max Planck Coal Research Institute, Mulheim an der Ruhr) entitled "New Preparative Possibilities in Boron and Silicate Chemistry," which could have been placed, with equal justification, in the Inorganic Section. Of the papers devoted to organic synthesis we may note one other communication, which was made by G. Drefahl (Friedrich Schiller University, Jena, German Democratic Republic) on the subject "Addition of Acetyl Nitrate to Olefins." The action of acetyl nitrate or a mixture of nitric acid and acetic anhydride on olefins results in the formation of the corresponding acetyl nitro compounds, the reduction of which gives acetyl derivatives of amino alcohols.

It is of interest to note the application of radioactive isotopes in biochemical investigations. Papers in this field were given by G. Kellner, L. Stockinger, B. Figdor, O. Suschny, R. Ukusik, and E. Broda (Vienna University) ("Investigations with Radioactive Carbon on Cultures of Cancerous Tissues") and by A. Becker (Organic Institute, Berlin Technical University, Charlottenburg) ("Cause of the Stability of Bacteria. Investigation with Radioactively Labeled Compounds").

Papers on natural organic compounds were given by A. Butenandt and coworkers (Max Planck Biochemical Institute, Tübingen) (on coloring matters) and by W. Pfleiderer (Technical High School, Stuttgart) (on the structure of urea).

It will be seen from our short review, which does not cover the whole of the work of the congress, that a wide range of chemical problems was discussed.

Having spent three days in Salzburg, on April 29, we went to Vienna, where we stayed until May 4, visiting the chemical laboratories of the university and technical high school and conversing with researchers and professors. We were interested in the organization of scientific and teaching work and in the equipment of the laboratories. Chemical research in Austria is carried out mainly in higher technical teaching establishments and in universities. At Vienna University we conversed with Professor E. Broda and Dr. T. Schönfeld, who work on radiochemistry, with Professor I. Breitenbach — a specialist in macromolecular chemistry — and Professor O. Gromatka, the director of the organic section of the First Chemical Laboratory, Vienna University. We made ourselves acquainted with the objects of the research work going on in these laboratories, with the teaching syllabuses, and with the organization of the practical work of students on physical and organic chemistry.

In Vienna Technical High School we inspected the Institute of Inorganic Chemical Technology (Director, Professor Hans Hohn), the Institute of Inorganic and Analytical Chemistry (Director, Professor Streubinger), and the Institute of Organic Chemistry (Director, Professor Waldmann).

In the Institute of Inorganic Technology extensive investigations are being carried out on solutions, metallic systems, and particularly on amalgams. Under the general supervision of Professor Hohn, investigations are proceeding on the preparation of pure metals (zinc, aluminum, lead, manganese and others) by electrolysis with a mercury cathode, and also on the preparation of sodium oxalate from carbon dioxide in presence of sodium amalgam. Dr. Franz Lihl is investigating the structure and properties of binary alloys obtained by the distillation of mercury from amalgams of the metals concerned or by coprecipitation at a mercury cathode. In this way the systems copper-nickel, copper-zinc, etc, have been investigated. Work on corrosion is being carried out by Professor H. Hohn in collaboration with Dr. E. Fitzer. W. Gutmann is studying the properties of nonaqueous solutions.

The Organic Chemistry Laboratory of the Technical High School is at present being refitted, and part of it is already completed. The walls, ceiling, floor and benches are all covered with a composition that is resistant to acids, alkalies, and organic solvents. The benches are movable , and the water, gas, and drain pipes are not mounted in the walls, but are fixed at a certain distance from them. This arrangement facilitates the inspection and repair of the gas, water and drainage systems.

During our stay in Austria, we were treated most attentively and cordially by the scientists; they willingly showed us their laboratories, told us about their investigations, and gave us reprints of their papers.

We received great help and attention from Professor Fritz Wessely, a prominent Austrian chemist who is President of the Second Chemical Institute of Vienna University and editor of Monatshefte für Chemie. He made us acquainted with the organization of the work of the congress.

We are very grateful also to Professor H. Hohn, who kindly acquainted us with the work going on in his laboratories, to Professor E. Broda, who assisted us in our inspection of the university laboratories, to Professors Streubinger and Waldmann, who showed us their laboratories and to several other Austrian chemists.

The Austrian scientists with whom we conversed showed a great interest in the Soviet Union, in the organization of scientific work in our country, and in the scientific literature that we publish.

M. A. Klochko

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INTERPHASE PARTITION IN SYSTEMS CONTAINING ANOMALOUS MIXED CRYSTALS

COMMUNICATION 5. THE SYSTEMS $NH_4Cl-CdCl_2-H_2O$ AND $NH_4Cl-NiCl_2-H_2O$

E. M. Ioffe

Study of the partition of a microcomponent between liquid and solid phases in systems consisting of ammonium and heavy-metal chlorides has revealed a marked difference in behavior between ter- and bi-valent metals [1]. Whereas in the systems $NH_4Cl-FeCl_3-H_2O$ and $NH_4Cl-CrCl_3-H_2O$ there is a lower formation limit, which is indicated by a fall in the partition coefficient as the microcomponent concentration falls in the solution, in the systems $NH_4Cl-MnCl_2-H_2O$ and $NH_4Cl-CuCl_2-H_2O$ the partition coefficient remains constant in all concentration ranges that we have investigated. In previous investigations [1, 2] it was shown that the difference in partition behavior in these two groups of anomalous mixed crystals is very probably to be explained by the scheme proposed by Greenberg and Walden [3] for the system $NH_4Cl-MnCl_2-H_2O$.

The radius of the cadmium ion differs greatly from the radii of the manganese and copper ions, and Nikitin suggested that this fact must have its reflection in a marked difference in the character of partition in the system $NH_4Cl-CdCl_2-H_2O$. Moreover, as we know from the work of Kumakov and Egorov [4], in the system $NH_4Cl-NiCl_2-H_2O$ the "guest" component is the double salt $NH_4Cl \cdot NiCl_2 \cdot 2H_2O$, which differs in composition from the double salts in the systems containing manganese and copper ($2NH_4Cl \cdot MCl_2 \cdot 2H_2O$). Nikitin [1] suggested that in the nickel system partition between liquid and solid phases may conform to a type of partition found in the iron system, i.e. that the mixed crystals of ammonium and nickel chlorides may have a lower formation limit. All these considerations suggested the need for a study of partition in the systems $NH_4Cl-CdCl_2-H_2O$ and $NH_4Cl-NiCl_2-H_2O$.

We adopted the procedure developed by Khlopin and his school for the study of the partition of small amounts of a substance between solid and liquid phases. Crystallization was carried out from supersaturated solutions with rapid stirring. The system was studied at 0°. For the determination of the microcomponent in the solid phase, crystals were filtered off under suction after the experiment and were washed free from mother liquor with ammonium chloride solution which was saturated at 0° and was applied at that temperature. No cadmium or nickel impurity could be detected in the reagents by spectrum analysis.

The System $NH_4Cl-CdCl_2-H_2O$. We know of the existence of solid solutions of ammonium and cadmium chlorides from the work of Lehman [5], St. Kreutz [6], Gaubert [7], and others. Rooseboom [8] showed also that cubic mixed crystals containing a little cadmium salt separate from ammonium chloride solutions containing $CdCl_2$. We studied partition in this system for various concentrations of cadmium in the original solution and with precipitation of various relative amounts of solid phase. We used two methods of investigation: chemical and radiochemical. In the chemical method we determined cadmium as oxide in the crystals and in the original solution, and in the radiochemical method we used the radioactive cadmium isotope Cd^{115}, which has a half-life of 43 days. The β-radiation was measured with a Type B apparatus having a B_1 tube. The results are given in Table 1.

As will be seen from Table 1, in the first and second series of experiments (Cd concentrations in solution of $1.2 \cdot 10^{-1}$ and $6.1 \cdot 10^{-2}$ M), the crystals contain about 43% of the cadmium and the partition coefficient is 1.7. With a threefold reduction of the cadmium content of the original solution, the proportion passing into the crystals rises considerably to 65% and the partition coefficient rises correspondingly to 4.5. Further reduction of the cadmium concentration of the solution leads to further increase in the partition coefficient, namely, to 6.8 in

TABLE 1

Molar concentration of Cd in solution	Amount of: Cd in 1 ml of original solution (g)	Amount of: NH_4Cl in crystals (% on total amt)	Cd in crystals (% on total amt.)	D (according to crystals)	Method
$1.2 \cdot 10^{-1}$	0.0140	30	45.3	1.9	Radiometric
$1.5 \cdot 10^{-1}$	0.0170	30	35.5	1.3	"
$1.5 \cdot 10^{-1}$	0.0170	30	47.7	1.9	"
			Mean	1,7	
$6.1 \cdot 10^{-2}$	0.0069	30	40.9	1.6	Gravimetric
$6.1 \cdot 10^{-2}$	0.0069	30	35.3	1.3	"
$6.1 \cdot 10^{-2}$	0.0069	30	45.6	1.9	"
$6.1 \cdot 10^{-2}$	0.0069	30	35.5	1.3	"
$6.1 \cdot 10^{-2}$	0.0069	30	36.6	1.4	"
$6.1 \cdot 10^{-2}$	0.0069	30	41.3	1.7	"
$6.1 \cdot 10^{-2}$	0.0069	30	41.5	1.7	Radiometric
			Mean	1,7	
$1.9 \cdot 10^{-2}$	0.0021	30	66.3	4.6	Gravimetric
$1.9 \cdot 10^{-2}$	0.0021	30	65.0	4.3	"
			Mean	4,5	
$1.4 \cdot 10^{-2}$	0.0016	30	75.0	7.0	"
$1.2 \cdot 10^{-2}$	0.0014	30	74.3	6.8	Radiometric
$1.4 \cdot 10^{-2}$	0.0016	30	74.0	6.6	Gravimetric
			Mean	6,8	
$5.6 \cdot 10^{-3}$	0.00063	30	79.6	9.1	Gravimetric
$6.1 \cdot 10^{-3}$	0.00069	30	80.0	9.3	Radiometric
$6.1 \cdot 10^{-3}$	0.00069	30	80.0	9.3	"
			Mean	9,3	
$3.7 \cdot 10^{-3}$	0.00042	30	83.2	11.5	Gravimetric
$3.7 \cdot 10^{-3}$	0.00042	30	83.0	11.2	"
$3.7 \cdot 10^{-3}$	0.00042	30	83.8	11.3	"
			Mean	11,3	
$2.2 \cdot 10^{-3}$	0.00033	30	94.6	78.8	"
$2.2 \cdot 10^{-3}$	0.00022	30	100		"
$2.2 \cdot 10^{-3}$	0.00022	30	100		"
$1.1 \cdot 10^{-3}$	0.00012	30	100		Radiometric

the fourth series of experiments, to 9.3 in the fifth, to 11.3 in the sixth, and to 78.8 in the seventh. Further reduction of the cadmium concentration to $2.9 \cdot 10^{-3}$ and $1.1 \cdot 10^{-3}$ M results in the passage of almost the whole of the cadmium into the crystals. Hence, as the cadmium concentration of the solution changes from $1.2 \cdot 10^{-1}$ to $1.1 \cdot 10^{-3}$ M, the partition coefficient, originally 1.7, rises regularly and tends to infinity. The whole of the cadmium found in the crystals after the experiment must be accounted for by the process of cocrystallization, for special experiments showed that the washings obtained by treating the crystals after the experiment with ammonium chloride solution saturated at 0° contained not more than 0.2% of the total amount of cadmium taken, so that the amount adsorbed on the crystal surface must have been negligible. Experiments that we carried out with a solution containing cadmium at a concentration of $5.2 \cdot 10^{-3}$ M showed that for this concentration Khopin's law

is applicable to the system, for with change in the amount of solid phase from 25 to 40% the partition coefficient remained constant (Table 2).

TABLE 2

Molar concentration of Cd in solution	Amount of: Cd in 1 ml of original solution (g)	Amount of: NH_4Cl in crystals (% on total amt)	Amount of: Cd in crystals (% on total amt.)	D	Method
$5.2 \cdot 10^{-2}$	0.0059	25	52.9	3.4	Gravimetric
$5.2 \cdot 10^{-2}$	0.0059	40	69.7	3.3	"

TABLE 3

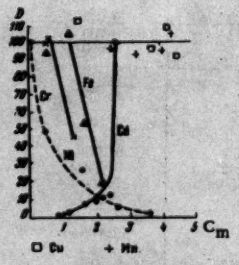
Molar concentration of Ni in original solution	Amount of: Ni in 1 ml of original solution	Amount of: NH_4Cl in crystals (% on total amount)	Ni in crystals (% on total amount)	D
$6.5 \cdot 10^{-1}$	$3.8 \cdot 10^{-2}$	30	6.0	0.14
$6.5 \cdot 10^{-1}$	$3.8 \cdot 10^{-2}$	30	7.1	0.17
			Mean	0.15
$2.6 \cdot 10^{-1}$	$1.5 \cdot 10^{-2}$	30	3.2	0.08
$2.6 \cdot 10^{-1}$	$1.5 \cdot 10^{-2}$	30	3.0	0.08
$2.6 \cdot 10^{-1}$	$1.5 \cdot 10^{-2}$	30	2.7	0.07
			Mean	0.08
$2.6 \cdot 10^{-2}$	$1.5 \cdot 10^{-3}$	30	1.8	0.042
$2.6 \cdot 10^{-2}$	$1.5 \cdot 10^{-3}$	30	2.2	0.050
$2.6 \cdot 10^{-2}$	$1.5 \cdot 10^{-3}$	30	1.7	0.040
			Mean	0.044
$5.2 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	30	1.1	0.026
$2.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	30	0.37	0.0086
$2.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	30	0.42	0.0098
$2.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	30	0.50	0.011
			Mean	0.0098
$2.6 \cdot 10^{-4}$	$1.5 \cdot 10^{-5}$	30	0.17	0.0040
$2.6 \cdot 10^{-4}$	$1.5 \cdot 10^{-5}$	30	0.19	0.0044
				0.0042

The System $NH_4Cl-NiCl_2-H_2O$. This system has been known since the time of Lehman, who found that it belongs to the iron–ammonium chloride type of anomalous solid solutions. The colored cubes that separate from solution show strong birefringence and appreciable pleochroism. Later, the fact that ammonium and nickel chlorides form mixed crystals was confirmed by several author, of whom we may mention Foot and Saxton [9,10]

and Clendinnen [11]. The most detailed investigation of this system was carried out by Kumakov and Egorov [4], who, after studying the solubility isotherms of this system at 0, 25, and 50°, concluded that the yellow coloration of ammonium chloride crystals depends on the presence of microdispersed inclusions of a dihydrate of a nickel carnallite of composition $NH_4Cl \cdot NiCl_2 \cdot 2H_2O$. As we have already stated, this fact prompted us to study the partition of nickel chloride between the crystals and a saturated ammonium chloride solution. The nickel contents of the original solution and of the crystals were determined by the Chugaev-Brunk method of precipitating nickel with alcoholic dimethylglyoxime. The results are given in Table 3.

As will be seen from Table 3, in the first series of experiments, in which the nickel concentration of the original solution is $6.5 \cdot 10^{-1}$ M, for precipitation of 30% of the ammonium chloride, the crystals contain, on the average, 6.5% of the nickel and the partition coefficient is 0.15.

In the second series of experiments, in which the nickel concentration of the original solution was reduced by a factor of 2.5, the proportion of the nickel passing into the crystals was reduced by about one-half and the partition coefficient was reduced correspondingly to 0.08. In the third series, with a reduction of the nickel concentration to one-tenth of its value in the preceding series, the partition coefficient fell to 0.044, and for a concentration of $5.2 \cdot 10^{-2}$ M it was already 0.026. In the fifth series it had a mean value of 0.0098, and in the sixth series, for a nickel concentration in the solution of $2.6 \cdot 10^{-4}$ M, it was reduced to 0.0042. Hence, with change in the nickel concentration in the original solution from $6.5 \cdot 10^{-1}$ to $2.6 \cdot 10^{-4}$ M, the partition coefficient is reduced from 0.15 to 0.0042, i.e., by a factor of about 36. The fall in the partition coefficient with reduction in the nickel concentration of the solution indicates the existence of a lower formation limit in this system, so that Nikitin's suggestion [1] is completely substantiated. We see, in fact, that in the nickel system the character of the partition of the microcomponent between solid and liquid phases is analogous to that found in the iron system, and that Greenberg and Walden's scheme, which satisfactorily explains the partition behavior of manganese and copper, is quite inapplicable to the system $NH_4Cl-NiCl_2-H_2O$. In this example we have once more found convincing evidence of the important part played by complex formation in systems containing anomalous mixed crystals. In order to compare the behavior of the systems $NH_4Cl-CdCl_2-H_2O$ and $NH_4Cl-NiCl_2-H_2O$ between themselves, and also with the manganese, copper, iron, and chromium systems that we have studied previously—we have plotted the negative logarithms of the molar concentrations of the microcomponent in the solution C_m as abscissas and the partition coefficients expressed as percentage of the maximum value for the given system as ordinates (see figure).



It will be seen from the figure that the mixed crystals formed by ammonium chloride with manganese and copper chlorides behave like true mixed crystals, for the value of the partition coefficient is here independent of the concentration of the microcomponent in the solution. The nickel system behaves like the ferric and chromic systems, for with reduction in the nickel concentration of the original solution the partition coefficient falls and tends to zero, just as in the iron and chromium systems; here, therefore, there is again a lower limit of formation. The cadmium system differs radically from all the other systems of ammonium and heavy-metal chlorides which we have studied, for in this case the partition coefficient increases with reduction in the cadmium concentration of the solution. Whereas the curves for the relation between partition coefficient and concentration of microcomponent in the solution are parallel to the axis of abscissas in the case of manganese and copper, they descend at an angle for iron, chromium, and nickel systems; in the case of the cadmium system, however, the curve moves upward. Other systems have been reported in the literature in which the partition of microcomponent between liquid and solid phases follows the pattern of the cadmium system.

For example, as early as 1932, Käding [12] found that lead (ThB) forms anomalous mixed crystals with alkali-metal halides, and it appeared to be characteristic of these that the partition coefficient rises as the lead concentration increases. The question of the mechanism of the formation of mixed crystals of this sort has not yet been resolved.

SUMMARY

1. The system $NH_4Cl-CdCl_2-H_2O$ differs radically from all previously studied systems formed by ammonium and heavy-metal chlorides, for in this case reduction in the cadmium concentration of the solution is associated with rise in the partition coefficient, which tends to infinity.

2. The system $NH_4Cl-NiCl_2-H_2O$ is similar to the analogous iron system, for reduction in the nickel concentration of the original solution is associated with a fall in the partition coefficient, which tends to zero. This indicates that the nickel system has a lower formation limit.

3. Greenberg and Walden's scheme, which satisfactorily explains the behavior of bivalent manganese and copper in their partition between crystals and saturated solution of ammonium chloride, is not applicable to the cadmium and nickel systems.

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ATTEMPT TO SET UP A SEMIQUANTITATIVE THEORY OF MUTUAL EFFECTS OF ATOMS IN ORGANIC COMPOUNDS

COMMUNICATION 2. ELECTRONIC CHARGES OF BONDS AND PHYSICAL PROPERTIES OF MOLECULES

G. V. Bykov

Force Constants and Characteristic Frequencies. In our first communication [1] we considered the calculation of σ-electronic charges in compounds not containing π-bonds. A knowledge of force constants and characteristic frequencies sometimes enables us to calculate total (σ- + π-) electronic charges of bonds. It is not possible to make very wide application of the methods of calculation which we are about to consider, but the results of their application are of fundamental importance and can provide basic data for calculations carried out by other methods.

The calculated values of force constants f obtained by various authors are not generally in agreement with one another. This is to be explained by the different simplifying assumptions that are made in the calculations. The most reliable values appear to be those obtained by Stepanov for simple molecules (Table 1).

TABLE 1

Force Constants, Characteristic Frequencies, and Electronic Charges of Bonds in Hydrocarbons

Hydrocarbon	Bond	f* (×10⁵ cm⁻²)	f** (×10⁵ dynes/cm)	A(f) (electrons)	ν*** (cm⁻¹)	A(ν) (electrons)
Methane	C—H	8.34	5.31	2.000	2914	2.000
Ethane	C—C	7.02	4.47	(2.272)****	993	(2.272)****
	C—H	8.08	5.14	(1.955)	2880	(1.955)
Ethylene	C—C	14.2	9.04	3.72	1623	4.10
	C—H	8.60	5.47	2.042	3019	2.095
Acetylene	C—C	~27	~17	~5.4	1974	5.18
	C—H	—	—	—	3371	2.445

* From results of Stepanov and Volkenshtein [2].

** The values of f given in this column were obtained from those in the preceding column by multiplication by the conversion factor $6.385 \cdot 10^{-5}$ g·cm²·sec⁻² [3].

*** From the latest edition of Landolt-Börnstein's Tables [4].

**** The values in parentheses are calculated from electronegativities (see [1]).

Fox and Martin found [5] that the energy of the C–C bond in saturated and unsaturated hydrocarbons varies as $f^{0.6}$. In the first communication we showed that there is direct proportionality between energies and σ-electronic charges of bonds. It is therefore rational to try, in the first place, the following equation for the relation between force constants and electronic charges of bonds:

$$f^m = \Delta' \cdot A. \qquad (1)$$

TABLE 2

Constants of Equations (1) and (2)

Bond	m	Δ^f	Δ^ν
C—C	(0.60)	$1.008 \cdot 10^3$	$1.737 \cdot 10^3$
C—H	0.70	$5.088 \cdot 10^3$	$3.553 \cdot 10^4$

Substituting f_{CC} (dynes/cm and A_{CC} for ethane in this formula and assuming, following Fox and Martin, that $m_{CC} = 0.6$, we may determine the proportionality coefficient Δ^f_{CH}. Substituting f_{CH} (dynes/cm) and A_{CH} for methane and ethane in Equation 1, we obtain two equations, which allow us to determine m_{CH} and Δ^f_{CH}. The results of these calculations are given in Table 2.

Using these constants, we calculated the total electronic charges A(f) of C−C in ethylene and acetylene and of C−H in ethylene from Equation 1 (Table 1, Column 5). In order to check the scheme of calculation we shall calculate the total electronic charge of the whole ethylene molecule:

$$\Sigma A(f) = 3.72 + 4 \cdot 2.042 = 11.89 \text{ electrons.}$$

The bonds in ethylene are made up of 12 valence electrons, so that the absolute error of calculation is 0,11 electron and the relative error is less than 1%. This indicates the possibility of apply Equation 1 also to unsaturated compounds.

In organic compounds, characteristic frequencies ν are possessed by bonds whose frequencies lie outside the frequency range of C−C bonds and are therefore relatively independent of the frequencies of other bonds and bond angles. The greater the difference between frequencies, the weaker the interaction between them. Hence, in the simplest hydrocarbons (ethane, ethylene, and acetylene) for example, the vibrations of C−C and C−H bonds are characteristic; to a first approximation they can be regarded as the vibrations of diatomic molecules and it may be supposed that ν^2 is proportional to f; taking Equation 1 into consideration we then obtain

$$\nu^{2m} = \Delta^\nu A, \qquad (2)$$

in which Δ^ν is a constant.

For the determination of Δ^ν_{CC} we shall use the frequency and charge of the C−C bond in ethane, and for the calculation of Δ^ν_{CH} the frequencies and charges of the C−H bonds in methane and ethane. The values obtained for the coefficients are given in the last column of Table 2. $\Delta^\nu_{CH} = 3.553 \cdot 10^4$ is the mean of two values, $3.542 \cdot 10^4$ and $3.564 \cdot 10^4$, obtained from the data for methane and ethane respectively.

The frequencies that we used for the calculation of Δ^ν correspond to the symmetrical vibrations of the bonds. Hence, in other calculations with these values of Δ^ν we may use only vibrations that are similar in form, i.e. symmetrical vibrations. Table 1 gives the frequencies ν of symmetrical vibrations and the values, calculated from these with the aid of Equation 2, of the total electronic charges $A(\nu)$ of the bonds in ethylene and acetylene. That the results may be regarded as quite satisfactory can be seen from calculations of the total electronic charges of the ethylene and acetylene molecules. For ethylene

$$\Sigma A(\nu) = 4.10 + 4 \cdot 2.095 = 12.48 \text{ electrons}$$

instead of 12; the relative error is 4%.* For acetylene

$$\Sigma A(\nu) = 5.18 + 2 \cdot 2.445 = 10.07 \text{ electrons}$$

instead of 10 electrons; the relative error is less than 1%.

The satisfactory results obtained in the calculation of m_{CH} and Δ^{ν}_{CH}, and also the closeness of the values A_{CH} in ethylene obtained by two different methods, indicate that the most reliable results are those for the electronic charges of C–H bonds calculated from Equations 1 and 2. It is therefore desirable to calculate the total electronic charges of C–C bonds in these compounds not directly from their force constants or vibrational frequencies, but from the difference between the number of valence electrons and ΣA_{CH}. With this method of calculation the total electronic charge of the C–C bond in acetylene is found to be $A_{CC} = 5.11$ electrons.

Knowing the total electronic charges of bonds, we may calculate the electronegativities of carbon atoms; in fact, according to Equation 1 of the first communication the total electronic charge of the C–H bond in acetylene is

$$A_{CH} = 1 + \frac{4 \cdot E_H}{E_H + E_C}.$$

so that $2.445 = 1 + \frac{4}{1 + E_C}$ and $E_C = 1.768$. Using this value of the electronegativity of carbon and applying the same Equation 1 of the first communication, we may calculate separately the σ- and π-electronic charges of C–C and C–H bonds in acetylene: $A^{\sigma}_{CC} = A^{\pi}_{CC} = 2.554$ electrons, $A^{\sigma}_{CH} = 1.723$ and $A^{\pi}_{CH} = 0.723$.

Bond Lengths. As is well known, the lengths of bonds having π-electronic charges are less than the lengths of the corresponding "pure" σ-bonds. The author, proceeding on the assumption that the shortening of a bond is proportional to its π-electronic charge,

$$L_{XY} - l_{XY} = \Delta^{l}_{XY} \cdot A^{\pi}_{XY}, \qquad (3)$$

carried out numerous calculations of π-electronic charges in hydrocarbons and their halogen derivatives, and also oxygen- and nitrogen-containing organic compounds [6, 7]. In Equation 3, L_{XY} is the length of a standard σ-bond, l_{XY} is the length of the given X–Y bond having a π-electronic charge of A^{π}_{XY}, and Δ^{l}_{XY} is the proportionality coefficient. In Table 3 we compare the results of calculations of π-electronic charges of bonds from Equation 3 and from Equation 1 of the first communication [1] together with Nekrasov's scale of relative electronegativities also cited in [1].

Table 3 gives the most typical organic compounds and bonds. There is on the whole close agreement between the results of the calculation of π-electronic charges by two methods that differ in principle.

Since my first calculations of π-electronic charges and bond lengths, i.e. 1951, much experimental material has accumulated which now enables us to calculate the constants L and Δ^{l} of Equation 3 with greater accuracy and to calculate or recalculate the π-electronic charges in a large number of organic compounds. Only after the completion of this work will there be a basis for an extensive comparison of the results of these two different methods of calculating π-electronic charges, and only then will it be desirable to come to conclusions concerning the π-electronic structure of ethylenic and aromatic compounds.

* It is possible that the choice of the frequency of the symmetrical vibration of the C–C bond may be incorrect, for if the frequency $\nu_{CC} = 1444$ is used in the calculation from Equation 2 we obtain $A_{CC}(\nu) = 3.56$ and $\Sigma A(\nu) = 11.94$ electrons, the relative error being 0.5%.

Additive Scheme for the Calculation of Heats of Formation of Unsaturated Hydrocarbons. As in the case of the additive scheme that we proposed in the first communication for the calculation of heats of formation of saturated hydrocarbons, we may write

$$\Delta_{CC}^{h\sigma}\cdot\Sigma A_{CC}^{\sigma}+\Delta_{CH}^{h\sigma}\Sigma A_{CH}^{\sigma}+\Delta_{CC}^{h\pi}\Sigma A_{CC}^{\pi}+\Delta_{CH}^{h\pi}\cdot\Sigma A_{CH}^{\pi}= \\ =H_{C_nH_m}^{el}+mL_H+4n\Delta_{CC}^{h\sigma}, \qquad (4)$$

in which $\Delta_{CC}^{h\sigma}$ and $\Delta_{CH}^{h\sigma}$ are the specific σ-electronic energies of C–C and C–H bonds respectively, $\Delta_{CC}^{h\pi}$ and $\Delta_{CH}^{h\pi}$ are the specific π-electronic energies of the C–C and C–H bonds, ΣA_{CC}^{σ} and ΣA_{CC}^{π} are summated σ- and π-electronic charges of C–C bonds, ΣA_{CH}^{σ} and ΣA_{CH}^{π} are the summated charges of C–H bonds, $H_{C_nH_m}^{el}$ is the heat of formation of the hydrocarbon C_nH_m from its elements, taken with the reverse sign, and L_H is the heat of atomization of hydrogen.

TABLE 3

Lengths and π-Electronic Charges of Bonds in Organic Compounds

Formula*	Bond	l	$A^{\pi}(l)$	$A^{\pi}(E)$	Δ_A
$H-C^{2\pi}-C^{2\pi}-H$	$C^{2\pi}-C^{2\pi}$	1.204	2.27	2.17 (2,55)**	−0.10 (+0.28)
	$C^{2\pi}-H$	1.057	0.86	0.91 (0.72)	+0.05 (−0.14)
$Cl-C^{2\pi}-C^{2\pi}-Cl$	$C^{2\pi}-C^{2\pi}$	1.195	2.32	1.82 (2.21)**	−0.50 (−0.11)
	$C^{2\pi}-Cl$	1.640	0.84	1.09 (0.89)	+0.25 (+0.05)
	$C^{\pi}-C^{\pi}$	1.330	1.42	0.75	−0.67
	$C^{\pi}-H$	1.087	0.14	0.31	+0.17
$C^{\pi}_6H_6$	$C^{\pi}-C^{\pi}$	1.40	0.95	0.70	−0.15
	$C^{\pi}-H$	—	0.05	0.30	+0.15
$C^{\pi}H_2-C^{\pi}HCl$	$C^{\pi}-Cl$	1.69	0.54	0.40	−0.14
$C^{\pi}_6H_5Cl$	$C^{\pi}-Cl$	1.69		0.38	−0.16
$>C^{\pi}-O^{\pi}$	$C^{\pi}-O^{\pi}$	1.22	1.40	1.44	+0.04
$C^{\pi}_6H_6(OH)_2$	$C^{\pi}-O$	1.36 Mean	0.47 Mean	0.46	−0.01
$X-C^{2\pi}-N^{2\pi}$	$C^{2\pi}-N^{2\pi}$	1.16 Mean	3.10 Mean	3.15	+0.05
	$C^{2\pi}-H$	1.057	0.86	0.74	−0.08
	$C^{2\pi}-Cl$	1.629	0.90	0.91	+0.01
	$C^{2\pi}-Br$	1.790	0.91	0.89	−0.02

* The index π attached to the symbol for an element indicates that the given atom is the donor of one π-electron; the index 2π indicates a donor of two π-electrons.

** The values in parentheses $A^{\pi}(E)$, are calculated from the electronegativity of acetylenic carbon $E_{C^{2\pi}}=1.768$.

We shall demonstrate the application of this scheme for the calculation of heats of formation and electronegativities for the case of alkynes. The figures obtained will in no sense have any final significance, since the experimental errors in the determination of the heats of formation of alkynes attain ± 0.5 kcal/mole. Nevertheless, some interesting inferences can be made from these figures.

For the calculation of the individual π-electronic energies $\Delta^{h\pi}_{CC}$ and $\Delta^{h\pi}_{CH}$, we shall use values of the heat of formation of 2-butyne and acetylene (Table 4). In 2-butyne $\Sigma A^{\pi}_{CH} = 0$ and $\Sigma A^{\pi}_{CC} = 4$.

We shall calculate the summated σ-electronic charges of C–C and C–H bonds in the way shown in the first communication, but taking into consideration that $E_{C^{2\pi}} = 1.768$. Substituting all numerical values in Equation 4, we obtain an equation with one unknown $\Delta^{h\pi}_{CC}$:

$$8{,}054 \cdot 6{,}966 + 32.308 \cdot 11{,}034 + \Delta^{h\pi}_{CC} \cdot 4 + \Delta^{h\pi}_{CH} \cdot 0 = \\ = -34.97 + 6 \cdot 52.089 + 4 \cdot 4 \cdot 8.054.$$

Substituting in Equation 4 the corresponding values for acetylene, including the value just calculated for $\Delta^{h\pi}_{CC}$, we can determine $\Delta^{h\pi}_{CH}$ (Table 5).

TABLE 4

Heat of Formation of Alkynes (with reversed sign)

Compound	Formula	$H^{el}_{C_nH_{2n-2}}$ *	Δ_H **
2-Butyne	$CH_3-C^{2\pi}-C^{2\pi}-CH_3$	−34.97	—
Acetylene	$H-C^{2\pi}-C^{2\pi}-H$	−54.194	—
Propyne	$H-C^{2\pi}-C^{2\pi}-CH_3$	−44.319	+0.54
1-Butyne	$H-C^{2\pi}-C^{2\pi}-CH_2-CH_3$	−39.48	+2.08
1-Pentyne	$H-C^{2\pi}-C^{2\pi}-CH_2-CH_2-CH_3$	−34.50	+2.66

* The values of heats of formation are taken from the work of Rossini and coworkers referred to in the first communication.

** $\Delta_H = H^{el}_{calc} - H^{el}_{expt}$.

TABLE 5

Specific Electronic Energies of C–C and C–H Bonds

Bond	$\Delta^{h\sigma}$	$\Delta^{h\pi}$
C–C	8.054	−1.54
C–H	32.308	−9.38

It is notable that the specific π-electronic energy is negative, and no possible corrections that may be made in the future in the experimental data can alter the negative value of $\Delta^{h\pi}_{CH}$. Hence, in spite of the fact that the total electronic charge of the C–H bond in acetylene is 2.445 electrons, which is more than in ethane (1.955 electrons), the energy of the $C^{2\pi}-H$ bond in acetylene, $D_{C^{2\pi}H} = 32.308 \cdot 1.723 - 9.38 \cdot 0.723 = 48.88$ kcal/mole, is less than the energy of the bond in ethane, $D_{CH} = 32.308 \cdot 1.955 = 63.16$ kcal/mole. This conclusion, however, will not appear paradoxical if we bring it into relation with the well known experimental fact that the protonization of hydrogen in acetylene proceeds much more readily than in ethane.

In Equation 4 let us substitute the corresponding numerical values for propyne, 1-butyne, and 1-pentyne calculated on the assumption that the electronegativity of a methyl or methylene carbon atom is $E_C = 1.19$. For propyne (Table 4) we obtain a discrepancy Δ_H between the calculated and experimental heats of formation which is quite of the same order as the experimental heats of formation which is quite of the same order as the experimental error. For the two succeeding hydrocarbons the discrepancy is considerably greater. This is not difficult to foresee. In fact, for the calculation of the heat of formation of propyne it is a matter of indifference what electronegativity we assume for the carbon of the methyl group, although a carbon directly attached to a highly negative acetylenic carbon must itself have high electronegativity. For the calculation of the heat of formation of 1-butyne, it is no longer a matter of indifference what electronegativity we assume for the carbon in the α-position to the acetylenic carbon, and this

enables us to estimate the electronegativity of the methylene carbon in this compound. In the calculation of the heat of formation of 1-butyne we obtained an error of $\Delta_H = +2.08$ kcal/mole. This error arises from the fact that we assigned too low a value to the electronegativity of the α-carbon atom with a resulting error in the calculation of the σ-electronic charge of the $C_\alpha - C_\beta$ bond and the three $C_\beta - H$ bonds of the methyl group. This error arose because, as we took took too low a value for the electronegativity of the α-carbon, the calculated summated σ-electronic charge of C–H bonds was too great by x electrons, and that of the C–C bonds was too small by the same amount; consequently:

$$8.054\,(\Sigma A^{\sigma}_{CC} - x) + 32.308\,(\Sigma A^{\sigma}_{CH} + x) = \\ = 8.054 \cdot \Sigma A^{\sigma}_{CC} + 32.308 \cdot \Sigma A^{\sigma}_{CH} + 2.08$$

or $-8.054x + 32.308x = 2.08$, so that $x = 0.086$. This error, which positive, is made in the calculation of the total σ-electronic charge of the three C–H bonds of the methyl group. For one bond the error is $\frac{x}{3} = 0.029$. As the σ-electronic charge of a C–H bond of a methyl group of a hydrocarbon is $1 + \frac{4}{3 + E_C}$ and we assumed in the original calculation that $E_C = 1.19$, it follows that

$$1 + \frac{4}{3 + 1.19} - 0.029 = 1 + \frac{4}{3 + y}$$

in which y is the required electronegativity of the α-carbon of 1-butyne. From this we find that $y = E_{C_\alpha} = 1.32$.* Using this value for the electronegativity of the α-methylene carbon in the calculation of the electronic charges in 1-pentyne and substituting the calculated values in Equation 4, we find that the error Δ_H is no longer + 2.86, but 1.40. An analogous, though somewhat more complex, calculation of the electronegativity of the β-methylene carbon in this compound gives $E_{C_\beta} = 1.25$.**

We have therefore obtained proof of the enhanced electronegativity of atoms directly attached to a more electronegative atom and of reduction in electronegativity as these atoms become further removed from the more electronegative atom.

Dipole Moments. In establishing the relation between electronic charges of bonds, on the one hand, and energies, force constants, characteristic frequencies, and lengths of bonds on the other, we started from the idea that these properties of bonds are mainly determined by the electronic charges of the bonds. However, we can sometimes state beforehand that this is not so, and our calculations will then provide only a rough estimate. Such calculations of dipole moments, which are carried out by an unusual method, yield very important results.

We will illustrate the method of calculating dipole moments for the case of propyne (see figure). We shall first calculate the dipole moment that arises from the fact that the σ-electronic charge of C–H bond is less than 2 electrons, whereas that of a $C-C^{3\pi}$ bond is greater than 2 electrons. One should imagine that this comes about by the transposition of a certain charge $\frac{1}{3}q$ from the middle of each of the three C–H bonds to the middle of the $C-C^{3\pi}$ bond. The vector sum of the three dipole moments arising in this way is directed along the axis $C-C^{3\pi}-C^{3\pi}$ and, as will be seen from the figure, is equal to $q\left(\frac{1}{2} l_{CH} \cdot \cos\alpha + \frac{1}{2} l_{CC^{3\pi}}\right)$, in which l_{CH} and $l_{CC^{3\pi}}$ are the C–H and $C-C^{3\pi}$ bond lengths. The transposed charge is the excess over one electron which the $C-C^{3\pi}$ bond obtained from four electrons of a C atom, i.e.

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* Strictly speaking, the value of E_{C_α} must be lower than this, for we are assuming that the electronegativity of carbon in a methyl group is 1.19, and, as we shall see later, this is not true. By assuming that overestimation of the summated σ-electronic charge of C–H bonds is due solely to underestimation of the value of E_{C_α}, we now overestimate the latter in our calculation.

** The heats of formation of 1-heptyne and higher normal homologs are at present calculated by the usual additive scheme with addition of 4.95 kcal/mole for each methylene group [8]. This is equivalent to assigning a value of 1.19 to the electronegativities of carbon atoms from γ–C, onward. This is evidently not true for γ-C, and it is probably not true for several more successive carbon atoms.

$$q = \frac{4 \cdot E_{C^{2\pi}}}{3 + E_{C^{2\pi}}} - 1 = \frac{3(E_{C^{2\pi}} - 1)}{3 + E_{C^{2\pi}}}.$$

The dipole moment of the methyl group in propyne is therefore

$$\mu_{CH_3C^{2\pi}} = \frac{3(E_{C^{2\pi}} - 1)}{2(3 + E_{C^{2\pi}})} (l_{CH} \cos\alpha + l_{CC^{2\pi}}).$$

The dipole moment calculated from this equation will be expressed in electron-angstroms; for conversion into debye units it must be multiplied by 4.8.

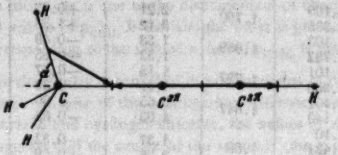

Diagram used in the calculation of the dipole moment of propyne. (The middles of the bonds are marked by short lines perpendicular to the bonds. The arrows indicate the transposition of electronic charges.)

In the general case – in place of $C^{2\pi}$ we may have any other atom X – the dipole moment arising owing to the transposition of σ-electronic charges from C–H bonds of the methyl group to the bond C–X is expressed (in debyes) by the equation

$$\mu_{CH_3X} = \frac{7.2(E_X - 1)}{3 + E_X} (l_{CH} \cdot \cos\alpha + l_{CX}). \qquad (5)$$

The dipole moments of monohalomethanes listed in Table 6 were calculated directly from this equation. In propyne, in accordance with the previous calculations, $E_{C^{2\pi}} = 1.77$. The angle α is the supplement of the tetrahedral angle 109°28'. Hence $\alpha = 70°32'$ and $\cos\alpha = 0.3333$. Data tables give $l_{CH} = 1.097$ and $l_{CC^{2\pi}} = 1.460$. Substituting these values in Equation 5 we obtain $\mu_{CH_3C^{2\pi}} = 2.13$ D.

The calculation of the dipole moments arising from the transposition of electronic charge from the middle of the acetylenic bond $C^{2\pi}-C^{2\pi}$ to the $C-C^{2\pi}$ and $C^{2\pi}-H$ bonds is still simpler. The excess above one electron that the $C^{2\pi}-H$ bond obtains from the four valence electrons of the $C^{2\pi}$ atom is equal to $\frac{4 \cdot E_H}{E_H + E_{C^{2\pi}}} - 1$, and the distance by which this charge is transposed is $\frac{1}{2} l_{C^{2\pi}H} + \frac{1}{2} l_{C^{2\pi}C^{2\pi}}$. Multiplication of the charge by this distance and the product by 4.8 gives the required dipole moment in debyes.

In the general case, for the structural element $X-C^{2\pi}-Y^{2\pi}$, in which $Y^{2\pi}$ may be $C^{2\pi}$ in an acetylenic bond or $N^{2\pi}$ in a nitrile bond, the dipole moment due to the passage of charge q from the bond $C^{2\pi}-Y^{2\pi}$ to the bond $X-C^{2\pi}$ is expressed in debyes by the equation

$$\mu_{Y^{2\pi}C^{2\pi}X} = 2{,}4\left(\frac{4E_X}{E_X+E_{Y^{2\pi}}}-1\right)(l_{XC^{2\pi}}+l_{C^{2\pi}Y^{2\pi}}). \qquad (6)$$

The dipole moments of hydrogen cyanide and cyanogen chloride (Table 6) were calculated from this equation.

TABLE 6

Dipole Moments, Experimentally Determined in the Gas Phase and Calculated

Formula	l**	p^{**}_{expt}	p_{calc}	Δ_p^{***}	E
CH_3F	CH 1.109 CF 1.385	1.790	2.21 3.12	+0.42 +1.33	1.85 2.31 F
CH_3Cl	CH 1.103 CCl 1.782	1.869	1.38 1.52	−0.49 −0.35	1.39 1.43 Cl
CH_3Br	CH 1.101 CBr 1.938	1.797	1.13 1.41	−0.67 −0.39	1.29 1.37 Br
CH_3I	CH 1.101 CJ 2.140	1.647	0.65 1.03	−1.00 −0.62	1.15 1.24 I
CH_3OH	CH 1.10 CO 1.421 OH 0.958	1.69	1.37 2.28	−0.32 +0.59	1.62 2.03 O
CH_3NH_2	CH 1.093 CN 1.47 NH 1.014	1.32	0.69 1.47	−0.63 +0.15	1.40 1.71 N
$CH_3C^{2\pi}C^{2\pi}H$	CH 1.097 $C^{2\pi}H$ 1.056 $CC^{2\pi}$ 1.460 $C^{2\pi}C^{2\pi}$ 1.207	0.75	0.00	−0.75	1.77 $C^{2\pi}$ 1.32 C
$N^{2\pi}C^{2\pi}H$	$C^{2\pi}H$ 1.064 $C^{2\pi}N^{2\pi}$ 1,156	3.00	2.53	−0.43	1.71 $N^{2\pi}$
$HC^{2\pi}C^{2\pi}Cl$	$C^{2\pi}H$ 1.052 $C^{2\pi}Cl$ 1.632 $C^{2\pi}C^{2\pi}$ 1.211	0.44	2.96	+2.52	1.43 Cl 1.77 $C^{2\pi}$
$N^{2\pi}C^{2\pi}Cl$	$C^{2\pi}Cl$ 1,629 $C^{2\pi}N^{2\pi}$ 1.163	2.80	5.51	+2.71	1.43 Cl 1.71 $N^{2\pi}$
$HC^{2\pi}C^{2\pi}Br$	$C^{2\pi}H$ 1.054 $C^{2\pi}Br$ 1.793 $C^{2\pi}C^{2\pi}$ 1.207	0.00	2,95	+2,95	1.37 Br 1.77 $C^{2\pi}$

* The formulas are written so that the calculated dipole moment is in the direction of the arrow, i.e., its negative end is to the right of the center of gravity of the positive charges of the molecule.

** Bond lengths l and experimental values of dipole moment p_{expt} are taken from the review of Gordy and coworkers [9] or, when there are no data in this, from the latest edition of Landolt-Börnstein [4]. The values of l in this table and in Table 3 are sometimes slightly different; for Table 3 other sources were used.

*** $\Delta_p = p_{calc} - p_{expt}$.

Substituting the values of $\underline{l}$ and E for propyne in this equation, we obtain $\mu_{CC^{sp}} = 4.54$ D and $\mu_{C^{sp}H} = 2.41$ D. Of the component moments, $\mu_{CH_3C^{sp}}$ and $\mu_{C^{sp}H}$ are directed in one direction, and $\mu_{CC^{sp}}$ – in the opposite direction. Hence, taking the directions of the individual dipoles into account, for the resultant dipole moment of propyne we obtain

$$p = \mu_{CH_3C^{sp}} - \mu_{CC^{sp}} + \mu_{C^{sp}H} = 2.13 - 4.54 + 2.41 = 0.00.$$

Similar, sometimes somewhat more complicated, calculations are required to obtain the other dipole moments given in Column 4 of Table 6.

As p_{calc} is very greatly dependent on E (for the first six examples $\frac{dp}{dE} = 3$, on the average), the electronegatives that were assumed in the calculation of a given value of $\underline{p}$ are given in Column 6 of Table 6. The upper of the bracketed values corresponds to the Gordy scale, and lower to the Nekrasov scale (see Communication 1).

As will be seen from the first six examples, p_{expt} and p_{calc} are close in value. It follows that the dipole moments of polyatomic molecules arise mainly from the nonintegral character of the electronic charges of the separate bonds. It is natural to expect that, in such molecules, p_{calc} will be less than p_{expt}, for a part of the over-all dipole moment of the molecule is due to the displacement of charges along individual bonds. In cases in which one of the tabulated values of p_{calc} is less and the other is greater than p_{expt}, it must be considered that the electronegativity corresponding to the second value of p_{calc} is the less probable.

The calculated and experimentally determined dipole moments of propyne and hydrogen cyanide also stand in the correct relationship. In spite of the considerable difference between the experimental values of the dipole moments of chloroacetylene and cyanogen chloride, the values of Δ_p for the two compounds are very close to one another. This suggests that the source of the anomaly (the high value of Δ_p and its positive charge) is the chlorine atom, the free electron pair of which is probably greatly displaced in the direction of the highly electronegative carbon atom C^{sp}. If this is so, then for the analogous bromine and iodine compounds Δ_p should be still greater. For bromoacetylene Δ_p is in fact greater than for chloroacetylene.

* * *

The other electrical properties and many of the other physical characteristics of molecules and individual bonds are also determined – mainly or in high degree – by the distribution of electronic charges among the bonds. For these, therefore, relationships can be established in the same way as we have established relationships for heats of formation, characteristic frequencies, bond lengths, and dipole moments. For example, for the calculation of molecular refractions we may propose an additive scheme similar to that for heats of formation, though it is true that it would be applicable to a more limited range of compounds. However, there is no need to discuss these matters, for, as far as the physical properties of molecules are concerned, we have illustrated the basic ideas of the theory.

SUMMARY

1. Simple semiempirical equations are proposed for the relation between force constants and characteristic frequencies of bonds on the one hand and total (σ- + π-) electronic charges of bonds on the other. These equations are checked by calculation of the total electronic charges of ethylene and acetylene. The electronegativity of acetylenic carbon is determined.

2. It is shown that it is possible to calculate π-electronic charges of bonds by two methods which give closely agreeing results – from bond lengths and from electronegativities.

3. An additive scheme is proposed for the calculation of heats of formation of unsaturated hydrocarbons from their elements; the scheme is analogous to that already proposed for saturated hydrocarbons. The separate π-electronic energies of C–C and C–H bonds are calculated. Electronegativities are calculated for carbon atoms in the α- and β-positions with respect to the acetylenic bond of normal 1-alkynes.

4. It is shown that dipole moments of polyatomic molecules are generally determined by the nonintegral character of the electronic charges of individual bonds. It is possible to estimate electronegativities of atoms from dipole moments.

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* Original Russian pagination. See C. B. Translation.

SYNTHESIS OF ORGANOSILICON COMPOUNDS CONTAINING CARBONYL AND CARBOXYL GROUPS

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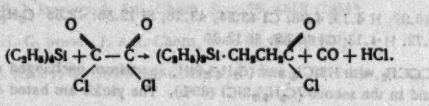
Organosilicon compounds containing carbonyl and carboxyl groups have generally been synthesized by the use of organometallic compounds, but papers have appeared recently on the synthesis of organosilicon acids by addition of silanes containing silicon-attached hydrogen to unsaturated esters with subsequent hydrolysis [1], the preparation of aldehydes and ketones by oxo synthesis with the aid of vinyl- and allyl-silanes [2], acylation of aromatic compounds with acid chlorides and fluorides in presence of $AlCl_3$ [3, 4], $SnCl_4$ [4], or BF_3 [5], and oxidation of p-ethylphenylsilanes [6].

We decided to try some new possible methods of preparing these compounds. As our first method we chose the known reaction of Kharasch for preparing aliphatic acid chlorides by reaction between oxalyl chloride $(COCl)_2$ and hydrocarbons in presence of a peroxide [7]. As organosilicon components for the reaction we used tetraethylsilane and chloro(ethyl)silanes. With $(C_2H_5)_4Si$ the reaction went satisfactorily and 3-(triethylsilyl)propionyl chloride was obtained in 32.2% yield on the amount of tetraethylsilane that reacted:



Apart from this product, small amounts of chlorotriethylsilane, dichlorodiethylsilane, and trichloroethylsilane were obtained.

Chlorotriethyl- and dichlorodiethyl-silanes also gave 3-substituted propionyl chlorides, but in lower yield. It must be mentioned that, in general, the yields of the acid chlorides were only 2-5% when reckoned on the amounts of reactants taken. In the case of trichloroethylsilane, the yield of acid chloride was so low that we did not succeed in isolating it.

As we wished to synthesize organosilicon acid chlorides having the functional group in the α-position, we brought $(C_2H_5)_3SiH$ and $HSiCl_3$ into reaction. In these cases, however, acid chlorides were not isolated and chlorotriethylsilane and silicon tetrachloride, respectively, were obtained in quantitative yields.

As our second method of synthesizing carbonyl-containing organosilicon compounds we selected the addition to vinylsilanes of aldehydes, and also of $HCCl_3$ and CCl_4, having in view the possibility of hydrolyzing the resulting (polychloroalkyl)silanes into acids. In the literature there is only a brief mention of the addition of butyraldehyde to trimethylvinylsilane without any indication of the yield of ketone [8]. We found that addition of butyraldehyde to triethylvinylsilane proceeds readily (60.2% yield), and with benzaldehyde the reaction again went satisfactorily. It is clear that this reaction can be used as a preparative method for obtaining organosilicon ketones in which the keto group is in the γ-position. Addition of $HCCl_3$ and CCl_4 to triethylvinylsilane in presence of a peroxide also went in good yield. Apart from the formation of the monomeric product, telomerization occurred with formation of an appreciable amount of high-boiling products containing Si and Cl. Unfortunately, we were unable to convert the resulting polychloroalkylsilanes by known methods [9, 10] into acids, for under the action of concentrated sulfuric acid at 100° quantitative carbonization occurred.

EXPERIMENTAL

1. Reaction of Tetraethylsilane and Chloroethylsilanes with $(COCl)_2$

A mixture of 91.5 g (0.635 mole) of $(C_2H_5)_4Si$ and 78.9 g (0.635 mole) of $(COCl)_2$ was prepared in a round-bottomed flask, and 1.5 g of freshly recrystallized benzoyl peroxide was added. Reaction began almost immediately, and the temperature of the mixture rapidly rose to 50°. The mixture was then heated at 70-90° for ten hours on each of three days, two further 1.5-g portions of benzoyl peroxide being added—one on the second, and one on the third day. Fractionation gave 11.3 g of oxalyl chloride, b.p. 64-66°; 0.7 g of trichloroethylsilane, b.p. 98-99° and n_D^{20} 1.4275; 0.9 g of dichlorodiethylsilane, b.p. 129° and n_D^{20} 1.4323; 2.8 g of chlorotriethylsilane, b.p. 143-144° and n_D^{20} 1.4315; 77.6 g of tetraethylsilane, b.p. 152-152.5° and n_D^{20} 1.4270; 7.4 g of benzoyl chloride, b.p. 75-77° (7 mm) and n_D^{20} 1.5528; and 6.4 g of 3-(triethylsilyl)propionyl chloride, b.p. 86-87.5° (5 mm); n_D^{20} 1.4449; d_4^{20} 0.9453; found MR 57.99; calculated MR 57.9. The yield, calculated on the amount of tetraethylsilane that reacted, was 32.2%.

Found %: C 52.52; 52.58; H 9.13; 9.04; Cl 16.07; 16.22; Si 13.52; 13.44 $C_9H_{19}SiOCl$.
Calculated %: C 52.42; H 9.22; Cl 16.99; Si 13.59

The reactions of $(COCl)_2$ with chlorotriethylsilane, dichlorodiethylsilane, and trichloroethylsilane were carried out under the same conditions. In the first two cases, apart from unchanged reactants and chloroethylsilanes, we isolated, respectively:

a) 3-(chlorodiethylsilyl)propionyl chloride, b.p. 87-88° (3.5 mm); n_D^{20} 1.4735; d_4^{20} 1.1321; found MR 52.82; calculated MR 53.03; the yield on the amount of $(C_2H_5)_3SiCl$ that reacted was 24.1%;

Found %: C 39.90; 39.92; H 6.96; 6.99, Cl 32.69; 33.06 $C_7H_{14}SiOCl_2$. Calculated %: C39.25; H 7.00; Cl 33.17

b) 3-(dichloroethylsilyl)propionyl chloride, b.p. 93-95° (6 mm); n_D^{20} 1.4820; d_4^{20} 1.2738; found MR 48.78; calculated MR 48.27; the yield on the amount of $(C_2H_5)_2SiCl_2$ that reacted was 11.7%;

Found %: C 31.01; 30.99; H 4.19; 4.38; Cl 43.54; 43.10; Si 12.55; 12.65 $C_5H_9SiOCl_3$.
Calculated %: C 30.72; H 4.13; Cl 44.55; Si 12.80

In the reactions of $(COCl)_2$ with $HSiCl_3$ and $(C_2H_5)_3SiH$, apart from unchanged reactants, in the first case was isolated $SiCl_4$ (71%), and in the second $(C_2H_5)_3SiCl$ (65%). The yields are based on the amount of the silane that reacted.

2. Reaction of Aldehydes with Triethylvinylsilane

A. Butyraldehyde. A mixture of 30.5 g (0.21 mole) of triethylvinylsilane and 62 g (0.87 mole) of butyraldehyde was prepared in the apparatus described above. It was heated at the boil for 50 hours, and at regular intervals 0.5-g portions of benzoyl peroxide were added so that 6 g was added in all. The boiling point of the mixture rose from 82° at the beginning to 121° at the end of the reaction. Fractionation gave 52.1 g of butyraldehyde, b.p. 74-76° and n_D^{20} 1.4834; 8.6 g of triethylvinylsilane, b.p. 145-146° and n_D^{20} 1.4332; and 19.9 g of 1-(triethylsilyl)-3-hexanone, b.p. 103.5° (3 mm); n_D^{20} 1.4560; d_4^{20} 0.8668; found MR 67.01; calculated MR 67.34; m.p. of semicarbazone 139°. The yield was 60.2% on the amount of triethylvinylsilane that reacted and 43.3% on the amount taken.

Found %: C 66.96; 67.20; H 12.10; 11.95 $C_{12}H_{26}SiO$. Calculated %: C 67.28; H 12.20

B. Benzaldehyde. The reaction conditions were the same. The reactants were 10 g (0.70 mole)* of triethylvinylsilane and 35.5 g (2.8 moles)* of benzaldehyde. The boiling point of the mixture rose from 156° to 177°. Fractionation gave 4.3 g of 3-(triethylsilyl)propiophenone, b.p. 168-170° (5 mm); n_D^{20} 1.5155; d_4^{20} 0.9746; found MR 76.71; calculated MR 76.36; m.p. of 2,4-dinitrophenylhydrazone 153°. The yield was 35% on the amount of triethylvinylsilane that reacted and 23% on the amount taken.

Found %: C 72.32; 72.38; H 9.80; 9.54 $C_{15}H_{24}SiO$. Calculated %: C 72.58; H 9.68

3. Reaction of CCl_4 and of $CHCl_3$ with Triethylvinylsilane

A. $CHCl_3$. The reaction conditions were the same. The reactants were 14.2 g (0.1 mole) of triethylvinylsilane and 46.8 g (0.4 mole) of $CHCl_3$. In the course of 30 hours 3 g of benzoyl chloride was added. The boiling

* Here, as elsewhere in the text, there are discrepancies between grams and moles of the given substances. These have not been corrected in translation — Publisher's note.

point of the mixture rose from 80° to 120°. Fractionation gave 12.8 g (48%) of triethyl(3, 3, 3-trichloropropyl) silane, b.p. 115-117° (3 mm); n_D^{20} 1.4785; d_4^{20} 1.0857; found MR 68.00; calculated MR 67.90. Yield 48%.

Found %: C 41.19; 41.03; H 7.01; 7.03; Cl 39.54; 39.48; Si 10.94; 10.74 $C_9H_{19}SiCl_3$.
Calculated %: C 41.60; H 7.32; Cl 40.50; Si 10.78

B. CCl_4. The reaction conditions were the same. Reaction was between 14.2 g (0.1 mole) of triethylvinylsilane and 29.1 g (0.4 mole) of CCl_4. In the course of 50 hours 5.5 g of benzoyl chloride was added. The boiling point of the mixutre rose from 84° to 103°. Fractionation gave 12.9 g (43.5%) of triethyl(1, 3, 3, 3-tetrachloropropyl)silane, b.p. 137-139° (5 mm); n_D^{20} 1.4974; d_4^{20} 1.2134; found MR 69.77; calculated MR 70.18.

Found %: C 36.47; 36.29; H 5.58; 5.77; Cl 47.78; 47.52; Si 9.58; 9.74 $C_9H_{18}SiCl_4$. Calculated %: C 36.88; H 6.13; Cl 47.57; Si 9.52

SUMMARY

1. Kharasch's addition reaction of aldehydes, $CHCl_3$, and CCl_4 was carried out with triethylvinylsilane, and his method of replacing hydrogen by the chloroformyl group was applied to tetraethylsilane and the chloro-(ethyl)silanes.

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POLYENIC COMPOUNDS

COMMUNICATION 2. POLYENIC COMPOUNDS CONTAINING HETEROCYCLIC SUBSTITUENTS

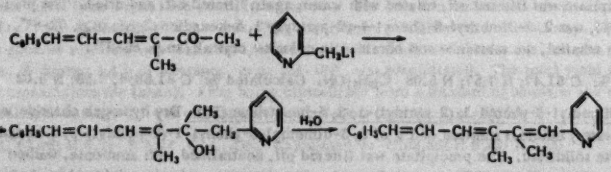
B. M. Mikhailov and G. S. Ter-Sarkisyan

In the preceding communication [1], which was devoted to the synthesis of hexatriene hydrocarbons, it was shown that phenyl- and 1-naphthyllithiums add to 3-methyl-6-phenyl-3, 5-hexadien-2-one at the 1, 2-positions of the conjugated system with formation of the corresponding tertiary alcohols, whereas addition of 9-fluorenyllithium occurs at the 1, 6-positions of the conjugated system and results in the formation of an unsaturated ketone. In continuation of these investigations we have now studied the reactions of the same ketone with 2-pyridylmethyllithium and with 2-quinolylmethyllithium.

An analogy might be expected between the behavior of the metal derivatives of 2-picoline, quinaldine, and fluorene toward unsaturated ketones, for these heterocyclic compounds and fluorene behave very similarly in many chemical reactions. Investigation showed, however, that 2-pyridyl- and 2-quinolyl-methyllithiums behave like aryllithiums toward 3-methyl-6-phenyl-3, 5-hexadien-2-one, i.e., 1, 2-addition to the conjugated system occurs with formation of the corresponding tertiary alcohols, 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-3, 5-hexadien-2-ol (I) and 2, 3-dimethyl-6-phenyl-1-(2-quinolyl)-3, 5-hexadien-2-ol (II).

Our measurements of electrical conductivity of ethereal solutions of 2-pyridylmethyllithium, 2-quinolylmethyllithium, and 9-fluorenyllithium showed that both heterocyclic organolithium compounds have negligible conductivity, whereas the conductivity of 9-fluorenyllithium approaches that of triphenylmethyllithium. Hence, the heterocyclic organolithium compounds are only extremely slightly ionized in ethereal solution and must be regarded as homopolar compounds, whereas in 9-fluorenyllithium the carbon-metal bond is heteropolar. There can be no doubt that the difference between the behavior of 9-fluorenyllithium on the one hand and that of aryllithiums and heterocyclic organolithium compounds on the other toward unsaturated ketones is to be explained by the difference in the nature of the carbon-metal bonds in these compounds.

Dehydration of the tertiary alcohols containing heterocyclic substituents gave the corresponding hexatriene derivatives, 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-1, 3, 5-hexatriene (III) and 2, 3-dimethyl-6-phenyl-1-(2-quinolyl)-1, 3, 5-hexatriene (IV); in neither case was the formation of stereoisomers observed.

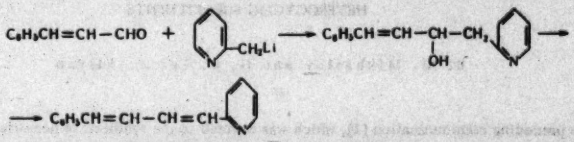


When an attempt was made to dehydrate 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-3, 5-hexadien-2-ol by heating it for 90 minutes at 150-160°, decomposition occurred with formation of 2-picoline and 3-methyl-6-phenyl-3, 5-hexadien-2-one, which was characterized as its 2, 4-dinitrophenylhydrazone. Similar decomposition

has been observed previously by Arens and coworkers [2] for the tertiary alcohol that they obtained from β-ionone and 4-methyl-2-pyridyllithium.

Apart from the above-described reactions, we investigated the reaction of 2-pyridylmethyllithium, and also of 2-quinolylmethyllithium, with cinnamaldehyde. It was found that in this case reaction proceeds readily with formation of 4-phenyl-1-(2-pyridyl)-3-buten-2-ol (V) and 4-phenyl-1-(2-quinolyl)-3-buten-2-ol (VI), which were obtained in satisfactory yields and without admixture of dehydration products.

When heated with glacial acetic acid, these alcohols lost water and were converted into the corresponding butadiene derivatives, 1-phenyl-4-(2-pyridyl)-1, 3-butadiene (VII) and 1-phenyl-4-(2-quinolyl)-1, 3-butadiene (VIII).



Some of these compounds have been prepared previously by other methods. Thus, 1-phenyl-4-(2-quinolyl)-1, 3-butadiene has been prepared by heating cinnamaldehyde with quinaldine and anhydrous zinc chloride [3-5] and also by the condensation of these reactants in presence of piperidine acetate [5]; in neither case was the yield high.

Späth and coworkers [6] tried to obtain the above-mentioned butenols by heating a mixture of equimolecular amounts of cinnamaldehyde and 2-picoline or quinaldine at 150-160° for 15-16 hours. In the case of 2-picoline they obtained the alcohol in admixture with the dehydration product, and in the case of quinaldine they could not isolate any butenol at all. The authors state that their 1-phenyl-4-(2-pyridyl)-1, 3-butadiene was a yellow substance. It is true that this substance remains yellow, even after several recrystallizations, and that under ultraviolet radiation it acquires a green fluorescence. However, by chromatography on alumina we succeeded in isolating 1-phenyl-4-(2-pyridyl)-1, 3-butadiene in the form of colorless crystals with a blue fluorescence.

When 4-phenyl-1-(2-pyridyl)-3-buten-2-ol was heated at 150-160°, decomposition was again observed, the products being 2-picoline and cinnamaldehyde.

EXPERIMENTAL

2, 3-Dimethyl-6-phenyl-1-(2-pyridyl)-3, 5-hexadien-2-ol (I). 2-Picoline (9.3 g, i.e., 0.1 mole) was added to a solution of phenyllithium prepared from 15.7 g (0.1 mole) of bromobenzene and 1.4 g of lithium in 100 ml of ether. The resulting solution of 2-pyridylmethyllithium was cooled, and after one hour an ethereal solution of 3-methyl-6-phenyl-3, 5-hexadien-2-one [7] was added; a crystalline precipitate rapidly began to form. The reaction mixture was stirred at room temperature for 90 minutes and was then set aside overnight. On the next day the precipitate was filtered off, treated with water, again filtered off, and dried. The product, amounting to 17.4 g (69.4%), was 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-3, 5-hexadien-2-ol, m.p. 72-81°. After being crystallized from ethanol, the substance was obtained in colorless crystals, m.p. 86-87°.

Found %: C 81.47; H 7.57; N 5.08 $C_{19}H_{21}ON$. Calculated %: C 81.68; H 7.53; N 5.02

2, 3-Dimethyl-6-phenyl-1-(2-pyridyl)-1, 3, 5-hexatriene (III). Dry hydrogen chloride was passed into a cooled (ice water) ethereal solution of 1 g of 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-3, 5-hexadien-2-ol until the precipitate solidified. The precipitate was filtered off, neutralized with ammonia, washed with water, and dried. The product, m.p. 97-99°, amounted to 0.9 g—an almost quantitative yield. After being crystallized from ethanol and subjected to chromatography on alumina, 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-1, 3, 5-hexatriene was obtained in the form of slightly yellowish crystals, m.p. 98-99°.

Found %: C 87.02; H 7.36; N 5.35 $C_{19}H_{19}N$. Calculated %: C 87.32; H 7.32; N 5.36

2, 3-Dimethyl-6-phenyl-1-(2-quinolyl)-3, 5-hexadien-2-ol (II). An ethereal solution of 3-methyl-6-phenyl-3, 5-hexadien-2-one was added over a period of one hour to a cooled solution of 2-quinolylmethyllithium prepared from 12.5 g (0.087 mole) of quinaldine and an equimolecular amount of phenyllithium. Toward the end of the addition the ketone was precipitated as yellow crystals. The reaction mixture was stirred for 3.5 hours at room temperature and then left overnight. On the next day the mixture was cooled with ice water, the ethereal solution was decanted, and the precipitate was decomposed with alcohol. The alcoholic solution was cooled with a cooling mixture and the precipitate that formed was filtered off, washed with water, and dried in a vacuum desiccator. In this way 11.7 g of 2, 3-dimethyl-6-phenyl-1-(2-quinolyl)-3, 5-hexadien-2-ol, m.p. 80-87°, was obtained, and by dilution of the alcoholic mother liquor with water a further 4.8 g of the same substance was obtained. The total yield was 16.5 g (59%). After being crystallized from ethanol, 2, 3-dimethyl-6-phenyl-1-(2-quinolyl)-3, 5-hexadien-2-ol was obtained as yellowish crystals, m.p. 88-90°.

Found %: C 83.83; H 6.93; N 4.25 $C_{23}H_{23}ON$. Calculated %: C 83.86; H 7.04; N 4.25

2, 3-Dimethyl-6-phenyl-1-(2-quinolyl)-1, 3, 5-hexatriene (IV). 2, 3-Dimethyl-6-phenyl-1-(2-quinolyl)-3, 5-hexadien-2-ol (3 g) was dehydrated under the conditions used in the previous dehydration experiment. The product, amounting to 2.4 g (85.6%), melted at 121-132°. After being crystallized from benzene and subjected to chromatography on alumina from a mixture of benzene and petroleum ether, 2, 3-dimethyl-6-phenyl-1-(2-quinolyl)-1, 3, 5-hexatriene was obtained in lemon-yellow crystals, m.p. 141-142°.

Found %: C 88.70; H 6.69; N 4.46 $C_{23}H_{21}N$. Calculated %: C 88.70; H 6.80; N 4.50

4-Phenyl-1-(2-pyridyl)-3-buten-2-ol (V). Cinnamaldehyde (11.9 g, i.e., 0.09 mole) was added to a cooled solution of 2-quinolylmethyllithium prepared as described above. The mixture was then stirred for 1 hour at room temperature and decomposed with water. In order to dissolve the precipitate that formed, ether was added. The ether layer was separated, solvent was distilled off, and the residue was steam-distilled to remove any unchanged reactants. The residual oil was extracted with benzene, solvent was distilled off, and the residue was treated with a 1:1 mixture of benzene and petroleum ether. The resulting crystalline precipitate was filtered off (12.6 g) and crystallized from aqueous methanol. In this way 4.8 g of 4-phenyl-1-(2-pyridyl)-3-buten-2-ol, m.p. 76-78°, was obtained, and from the mother liquor a further 4.5 g of the same substance, m.p. 74-78°, was obtained. The total yield was 9.3 g (45%). After being recrystallized from a mixture of benzene and ethanol, 4-phenyl-1-(2-pyridyl)-3-buten-2-ol was obtained as colorless crystals, m.p. 82-83° (the literature [6] gives 82-83°).

1-Phenyl-4-(2-pyridyl)-1, 3-butadiene (VII). A solution of 1 g of 4-phenyl-1-(2-pyridyl)-3-buten-2-ol in 4 ml of glacial acetic acid was boiled for five minutes with 0.5 ml of concentrated sulfuric acid, after which the solution was cooled, diluted with water, and neutralized with ammonia. The precipitate was filtered off, washed with water, and dried. The product was 0.88 g—an almost quantitative yield—of 1-phenyl-4-(2-pyridyl)-1, 3-butadiene, m.p. 110-116°. After being crystallized from a mixture of benzene and ethanol and then subjected to chromatography on alumina, 1-phenyl-4-(2-pyridyl)-1, 3-butadiene was obtained in colorless crystals, m.p. 123-124°; it showed blue fluorescence.

In the literature [6], this substance is described as yellow plates, m.p. 123-124°.

4-Phenyl-1-(2-quinolyl)-3-buten-2-ol (VI). An ethereal solution of 8.6 g (0.065 mole) of cinnamaldehyde was added to a cooled solution of 2-quinolylmethyllithium prepared from 10 g (0.07 mole) of freshly distilled quinaldine and an equimolecular amount of phenyllithium. Toward the end of the addition of cinnamaldehyde, the solution cleared and a little crystalline precipitate formed. The reaction mixture was boiled for one hour, and on the next day it was decomposed with water. The precipitate was filtered off (4.6 g, m.p. 125-131°). The ethereal and aqueous solutions were separated, ether was distilled off, and the residual oil was cooled with a cooling mixture. A further 1.4 g of substance, m.p. 124-130°, was precipitated. The total yield was 6 g (33.5% on the amount of cinnamaldehyde taken). After being crystallized from a mixture of benzene and ethanol, 4-phenyl-1-(2-quinolyl)-3-buten-2-ol was obtained as fine colorless crystals, m.p. 142°.

Found %: C 83.06; H 6.21; N 5.13 $C_{19}C_{17}ON$. Calculated %: C 82.88; H 6.22; N 5.09

1-Phenyl-4-(2-quinolyl)-1, 3-butadiene (VIII). 4-Phenyl-1-(2-quinolyl)-3-buten-2-ol (1 g) was dehydrated in the manner described above. The product, amounting to 0.74 g (83%), melted at 114-117°. After being crystallized from a mixture of benzene and ethanol and then subjected to chromatography on alumina from a 1:1 mixture of benzene and petroleum ether, 1-phenyl-4-(2-quinolyl)-1, 3-butadiene was obtained in light yellow crystals, m.p. 118-119° (the literature [6] gives 119°); it showed blue fluorescence.

SUMMARY

1. In the reactions of 2-pyridylmethyllithium and of 2-quinolylmethyllithium with 3-methyl-6-phenyl-3, 5-hexadien-2-one, the corresponding tertiary alcohols were formed. Dehydration of these gave 2, 3-dimethyl-6-phenyl-1-(2-pyridyl)-1, 3, 5-hexatriene and 2, 3-dimethyl-6-phenyl-1-(2-quinolyl)-1, 3, 5-hexatriene.

2. Reaction of 2-pyridylmethyllithium and of 2-quinolylmethyllithium with cinnamaldehyde gave the butenols 4-phenyl-1-(2-pyridyl)-3-buten-2-ol and 4-phenyl-1-(2-quinolyl)-3-buten-2-ol. Dehydration of these gave butadiene derivatives.

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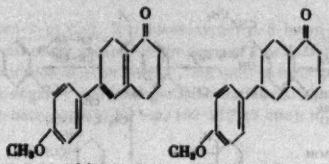
SYNTHESIS OF STEROID COMPOUNDS AND RELATED SUBSTANCES

COMMUNICATION 38. ANALOGS OF DOISYNOLIC ACID NOT CONTAINING A B RING

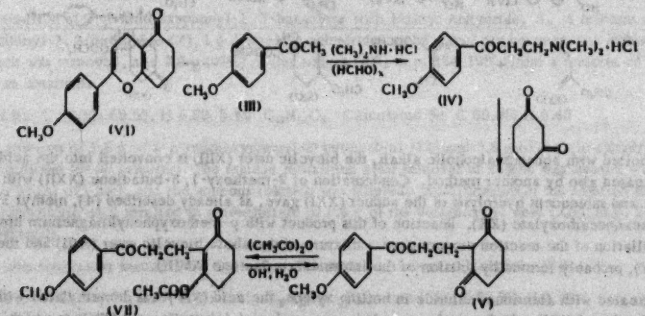
I. N. Nazarov and S. I. Zavyalov

In a previous investigation [1] we synthesized some tricyclic ketones of the types (I) and (II), which are structurally related to homoestrone with its B ring removed.



The present paper describes further synthetic work on structural analogs of steroid hormones.

By treatment with paraform and dimethylamine hydrochloride, 4'-methoxyacetophenone (III) was converted in good yield into the hydrochloride of 3-dimethylamino-4'-methoxypropiophenone (IV) [2], which reacted with 1, 3-cyclohexanedione in presence of alkali with formation of the triketone (V). Attempts to cyclize

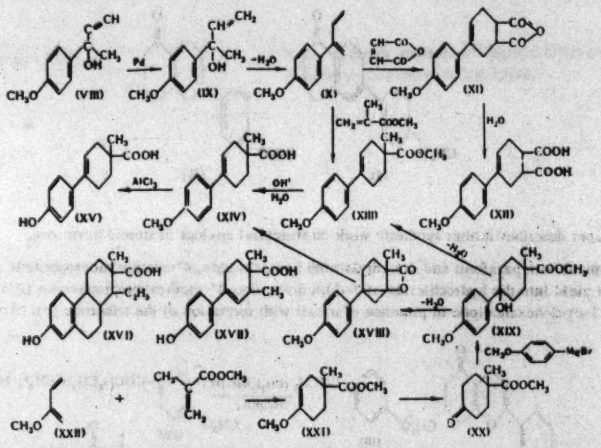


this product with the object of obtaining the oxygen-containing steroid analog (VI) were not successful, for treatment of the triketone (V) with phosphoric oxide or sulfuric acid did not yield any individual products, and treatment with boiling acetic anhydride in presence of sodium acetate gave the enol acetate (VII). When treated with alkali for a short time, this ester was hydrolyzed into the original triketone (V).

Reaction of 4'-methoxyacetophenone with acetylene by the method developed in our laboratory [3] gave the acetylenic alcohol (VIII), which was converted into the ethylenic alcohol (IX) when partially hydrogenated over a palladium catalyst. Dehydration of the ethylenic alcohol under various conditions (with the aid of potassium hydrogen sulfate, p-toluenesulfonic acid, or magnesium sulfate) was accompanied by much polymerization, and the highest yield of the diene (X) that we were able to attain was 35%. This diene readily underwent diene synthesis with maleic anhydride, and the adduct obtained (XI) was quantitatively hydrolyzed by alkali into the dicarboxylic acid (XII).

It was found that the ethylenic alcohol (IX) could be used directly in the diene condensation instead of the diene (X); dehydration of (IX) then occurred in the reaction itself. Thus, heating of the ethylenic alcohol (IX) with maleic anhydride or methacrylic acid in boiling xylene gave the corresponding adduct (XI) or (XIII) in a yield of 33% or 38%, respectively.

As in the condensation with maleic anhydride the above-mentioned dicarboxylic acid (XII) is formed as well as the adduct (XI); the total yield in this reaction attains 50%.



When boiled with aqueous-alcoholic alkali, the bicyclic ester (XIII) is converted into the acid (XIV), which we prepared also by another method. Condensation of 2-methoxy-1, 3-butadiene (XXII) with methyl methacrylate and subsequent hydrolysis of the adduct (XXI) gave, as already described [4], methyl 1-methyl-4-oxo-1-cyclohexanecarboxylate (XX). Reaction of this product with p-methoxyphenylmagnesium bromide and vacuum-distillation of the reaction product gave a mixture of the above bicyclic ester (XIII) and the corresponding acid (XIV), probably formed by scission of the intermediate lactone (XVIII).

When treated with aluminum chloride in boiling xylene, the acid (XIV) was demethylated with formation of the bicyclic phenol (XV), which may be regarded as an analog of doisynolic acid (XVI) in which the B ring is missing. It must be pointed out that the previously described [5] phenolic acid (XVII), which was prepared by another method, possesses estrogenic activity.

EXPERIMENTAL

Preparation of the Triketone (V). A mixture of 4.2 g of the hydrochloride of 3-dimethylamino-4'-methoxypropiophenone (IV) (m.p. 180-181°) [2], 3 g of 1, 3-cyclohexanedione (m.p. 104-105°) [6], and a solution of 1 g of potassium hydroxide in 20 ml of water was heated for 30 minutes in a boiling water bath. When cool, the solution was treated with 2 g of sodium carbonate, filtered, and acidified to Congo red with concentrated hydrochloric acid. Addition of ether to the precipitated oil caused it to crystallize, and 2.5 g (33%) of the triketone (V), m.p. 119-120° (from aqueous methanol), was obtained.

Found %: C 70.37; 70.23; H 6.51, 6.62 $C_{16}H_{18}O_4$. Calculated %: C 70.1; H 6.5

Reaction of the Triketone (V) with Acetic Anhydride. A mixture of 3 g of the triketone (V), 0.03 g of sodium acetate, and 24 ml of acetic anhydride was refluxed for three hours. Acetic acid and excess of acetic anhydride were removed, and the residue was treated with 1 g of sodium carbonate in 15 ml of water and then extracted with chloroform. The chloroform extract gave 1.5 g (44%) of the enol acetate (VII), b.p. 228-231° (1 mm) and n_D^{20} 1.5620.

Found %: C 68.19; 68.36; H 6.34; 6.39 $C_{18}H_{20}O_5$. Calculated %: C 68.3; H 6.3

Hydrolysis of the Enol Acetate (VII). A mixture of 1.5 g of the enol acetate (VII) and a solution of 0.4 g of potassium hydroxide in 10 ml of water was stirred at 60-70° until the oil dissolved (about 45 minutes). The cooled solution was acidified with hydrochloric acid, and 0.9 g (69%) of the triketone (V), m.p. 119-120°, was precipitated.

2-p-Methoxyphenyl-3-buten-2-ol (IX). 2-p-Methoxyphenyl-3-butyn-2-ol (VIII) (30 g; m.p. 35°) [3] was hydrogenated as a solution in 50 ml of dry dioxane in presence of a palladium catalyst supported on calcium carbonate (5% Pd). After the absorption of 4025 ml (18°, 755 mm) of hydrogen, i.e., one molecular equivalent, the test for an acetylene became negative and hydrogenation was discontinued. The product, amounting to 22 g (70%) was 2-p-methoxyphenyl-3-buten-2-ol (IX), b.p. 109-110° (2 mm); n_D^{20} 1.5393; d_4^{20} 1.056; found MR 52.82; calculated MR 52.1.

Found %: C 74.16; 74.10; H 7.99; 8.07 $C_{11}H_{14}O_2$. Calculated %: C 74.20; H 7.89

2-p-Methoxyphenyl-1, 3-butadiene (X). A mixture of 5 g of 2-p-methoxyphenyl-3-buten-2-ol (IX) and 5 mg of potassium hydrogen sulfate was heated under a residual pressure of 5 mm of nitrogen at a bath temperature of 100°. The product was dried with calcium chloride and distilled under a reduced pressure of nitrogen. The product, amounting to 1.5 g (35%), was 2-p-methoxyphenyl-1, 3-butadiene (X), b.p. 80° (3 mm); n_D^{20} 1.5554; d_4^{20} 0.934.

Found %: C 82.20; 81.97; H 7.63; 7.69 $C_{11}H_{12}O$. Calculated %: C 82.45; H 7.50

Condensation of 2-p-Methoxyphenyl-1, 3-butadiene with Maleic Anhydride. 1. A mixture of 1.7 g of 2-p-methoxyphenyl-1, 3-butadiene (X), 1 g of maleic anhydride, and 6 ml of dry benzene was refluxed for one hour. Solvent was removed, and 2.5 g (95%) of the adduct (XI), m.p. 124-125° (from a mixture of benzene and heptane), was obtained.

Found %: C 70.17; 69.93; H 5.69; 5.59 $C_{15}H_{14}O_4$. Calculated %: C 69.99; H 5.45

2. A solution of 1.8 g of 2-p-methoxyphenyl-3-buten-2-ol (IX) and 0.8 g of maleic anhydride in 16 ml of xylene was refluxed for 30 minutes. The residue remaining after removal of xylene was treated with 3 g of sodium carbonate in 20 ml of water, and the aqueous solution was filtered. Acidification of the solution to Congo red with 1:1 hydrochloric acid resulted in a precipitate of 0.4 g of the dicarboxylic acid (XII), m.p. 208-210° (from aqueous methanol).

Titration equivalent found: 140 $C_{15}H_{16}O_5$. Titration equivalent calculated: 138

Found %: C 65.11; 65.14; H 5.93; 5.91 $C_{15}H_{16}O_5$. Calculated %: C 65.22; H 5.88

The neutral product, after being recrystallized from a mixture of benzene and heptane, gave 0.8 g of the above-described adduct (XI), m.p. 124-125°. Conversion of the adduct (XI) into the dicarboxylic acid (XII) was effected in quantitative yield by a short hot treatment with dilute caustic alkali solution.

Preparation of Methyl 4-p-Methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylate (XIII). A mixture of 2.2 g of 2-p-methoxyphenyl-3-buten-2-ol (IX), 3 g of methyl methacrylate, and 15 ml of xylene was refluxed for four hours. Solvent was removed, and vacuum-distillation of the residue gave 1.2 g (37%) of methyl 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylate (XIII), b.p. 158-166° (1 mm) and n_D^{20} 1.5549.

Found %: C 73.54; 73.48; H 7.35; 7.46 $C_{16}H_{20}O_3$. Calculated %: C 73.8; H 7.7

Hydrolysis of Methyl 4-p-Methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylate (XIII). A mixture of 1 g of methyl 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylate (XIII) and a solution of 0.5 g of sodium hydroxide in 10 ml of 50% aqueous alcohol was refluxed for four hours. The mixture was cooled, diluted with 10 ml of water, and acidified with concentrated hydrochloric acid. A precipitate of 0.5 g (53%) of 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylic acid (XIV), m.p. 132-133° (from heptane), was obtained.

Titration equivalent found: 245 $C_{15}H_{18}O_3$. Titration equivalent calculated: 246

Found %: C 73.40; 73.05; H 7.29; 7.30 $C_{15}H_{18}O_3$. Calculated %: C 73.15; H 7.31

Reaction of p-Methoxyphenylmagnesium Bromide with Methyl 1-Methyl-4-oxo-1-cyclohexanecarboxylate (XX). The Grignard reagent prepared from 7 g of p-bromoanisole and 0.8 g of magnesium in 50 ml of ether was added dropwise to a stirred ice-cooled solution of 4.4 g of methyl 1-methyl-4-oxo-1-cyclohexanecarboxylate (XX) (b.p. 115-117° (14 mm); n_D^{20} 1.4618) [4] in 30 ml of ether. The mixture was allowed to stand for one hour at room temperature and was then decomposed with ice and dilute (1 : 1) hydrochloric acid. The ether layer was washed with sodium carbonate solution, and ether was evaporated off. Vacuum distillation of the residue gave 1.6 g of methyl 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylate (XII), b.p. 159-164° (1 mm) and 1.7 g of the acid (XIV), b.p. 185-200° (1 mm), m.p. 132-133° (from heptane).

Demethylation of 4-p-Methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylic acid (XIV). A mixture of 0.4 g of 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylic acid (XIV), 1 g of aluminum chloride, and 5 ml of xylene was refluxed for 5 minutes. The mixture was cooled and treated with ice and dilute hydrochloric acid. The precipitate formed was dissolved in sodium carbonate solution, and the resulting solution was boiled with activated charcoal and acidified with dilute hydrochloric acid. There was a precipitate of 0.12 g (33%) of 4-p-hydroxyphenyl-1-methyl-3-cyclohexene-1-carboxylic acid (XV), m.p. 167-168° (from water).

Found %: C 72.35; 72.17; H 6.74; 6.78 $C_{14}H_{16}O_3$. Calculated %: C 72.4; H 6.8

SUMMARY

1. Reaction between the hydrochloride of 3-dimethylamino-4'-methoxypropiophenone (IV) and 1, 3-cyclohexanedione in presence of alkali gave the bicyclic triketone (V), which was converted into the corresponding enol acetate (VII) when boiled with acetic anhydride in presence of sodium acetate.

2. It was shown that 2-p-methoxyphenyl-1, 3-butadiene (X) readily undergoes diene condensation with maleic anhydride and with methyl methacrylate with formation of the normal adducts (XI) and (XIII). It was found that in these reactions it is possible to use 2-p-methoxyphenyl-3-buten-2-ol directly, as it is readily dehydrated under the conditions of the experiment.

3. Reaction between p-methoxyphenylmagnesium bromide and methyl 1-methyl-4-oxo-1-cyclohexanecarboxylate (XX) gave a mixture of 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylic acid (XIV) and the corresponding ester (XIII), the products being identical with those obtained previously by diene condensation of 2-p-methoxyphenyl-1, 3-butadiene (X) with methyl methacrylate.

4. Demethylation of 4-p-methoxyphenyl-1-methyl-3-cyclohexene-1-carboxylic acid (XIV) by the aid of aluminum chloride in boiling xylene gave the bicyclic phenol (XV), which is of interest for tests on estrogenic activity.

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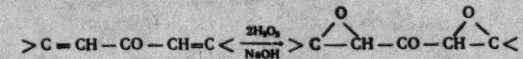
α-KETO EPOXIDES AND THEIR REACTIONS

COMMUNICATION 7. GEOMETRIC ISOMERISM IN THE α-KETO DIEPOXIDE SERIES

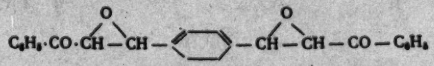
I. N. Nazarov and A. A. Arkhem

In a previous communication [1] we showed that aliphatic divinyl ketones are smoothly oxidized by alkaline hydrogen peroxide to the corresponding α-keto epoxides:



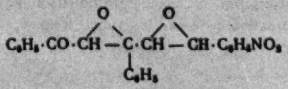
In the case of unsymmetrically substituted divinyl ketones the α-keto diepoxides may be obtained in the form of cis and trans isomers.

Weitz and Scheffer [2] were the first to suggest that 3, 3"-p-phenylenebis[23-epoxypropiophenone] (I), which they prepared, could exist in the form of three geometric isomers: cis-cis, cis-trans, and trans-trans. However, they did not isolate any of these isomers in the pure state.



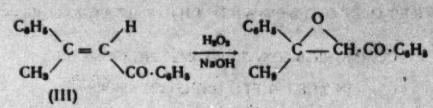
(I)

Somewhat earlier, Bodfon [3] condensed 2, 3-epoxy-3-m-nitrophenylpropiophenone with 2-bromoacetophenone and isolated two isomeric keto diepoxides (II), m.p. 170° and 207°, although other keto epoxides of this series had been obtained in one form only.



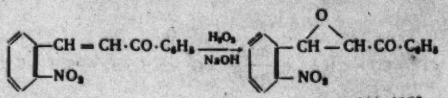
(II)

Apart from geometric isomerism, in this case the author admitted the possibility of physical isomerism—so-called monotropy. These are the only examples in the literature of cis-trans isomerism in the α-keto diepoxide series. Very little study has been devoted also to the stereochemistry of the oxidation of α, β-unsaturated ketones with alkaline hydrogen peroxide. Lutz [4] showed recently that oxidation of isomeric chalcones with alkaline hydrogen peroxide gave the corresponding α-keto epoxides only in the trans configuration. However, it is known also that dypnone (III), which is a chalcone derivative, gives two isomeric α-keto epoxides, m.p. 94° and 164°, under these conditions [5]:



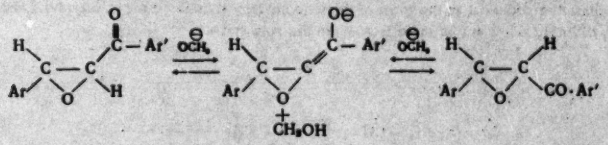
(III)

As Cromwell and Setterquist [6] showed, the α- and β-forms of 2, 3-epoxy-3-o-nitrophenylpropiophenone, m.p. 111° and 175°, which were obtained previously by Bodfon [7] are geometric isomers. They [6] synthesized the α-form of Bodfon's keto epoxide (m.p. 111°) by oxidation of 2-nitrochalcone with alkaline hydrogen peroxide:



m.p. 111-112°

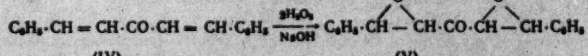
The isomerization of the α-form into the β-form in presence of sodium ethoxide, which was first observed by Bodfon [3], is explained by Cromwell and Setterquist [6] as follows:



trans (α) form cis (β) form

We studied the oxidation of 1, 5-diphenyl-3-pentadienone (IV), m.p. 112-113°, with alkaline hydrogen peroxide. The dienone was prepared by the alkaline condensation of benzaldehyde with acetone [8] and—on analogy with 4-phenyl-3-buten-2-one and chalcone, for which the trans configurations have been rigorously proved [4]—probably has a trans-trans configuration.

By the oxidation of 1, 5-diphenyl-3-pentadienone (IV) with alkaline hydrogen peroxide in dioxane, we obtained a quantitative yield of a crystalline α-keto diepoxide (V) in the form of a mixture of geometric isomers, from which fractional crystallization gave two individual isomers, m.p. 99° and 119°:

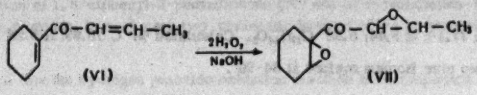


(IV) (V)

In addition we obtained an appreciable amount of an intermediate fraction, m.p. 86-110°, which we did not succeed in resolving into individual isomers. It should be noted that Weitz and Scheffer [2], in their attempt at oxidizing 1, 5-diphenyl-3-pentadienone (IV) with alkaline hydrogen peroxide, did not succeed in isolating the keto diepoxide (V).

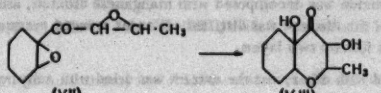
Our result indicates that, in the oxidation of 1, 5-diphenyl-3-pentadienone (IV) with alkaline hydrogen peroxide in dioxane, inversion of geometric configuration probably occurs, since at least two isomers of the α-keto diepoxide (V) are formed; this is in complete agreement with the ionic mechanism of this reaction [9].

Oxidation of 1-cyclohexen-1-yl propenyl ketone (VI) with alkaline hydrogen peroxide gave the keto diepoxide (VII) in a yield of about 70%. This again appears to exist in two geometric forms (liquid and solid):



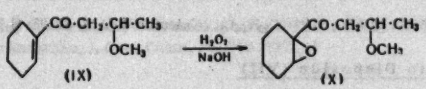
(VI) (VII)

Hydrolysis of the crystalline keto diepoxide (VII) with boiling water gave a crystalline dihydroxychromanone (VIII), and hydrolysis of the liquid diepoxide (VII) gave the chromanone (VIII) in the form of a viscous, difficulty crystallizable sirup:



(VII) (VIII)

Oxidation of the methoxy ketone (IX) with alkaline hydrogen peroxide gave the keto epoxide (X) in high yield:



(IX) (X)

It should be noted that the rate of oxidation of the dienone (VI) with alkaline hydrogen peroxide is appreciably greater than the rate of oxidation of the methoxy ketone (IX).

EXPERIMENTAL

α-Keto Diepoxide (V)

A solution of 105 g of 1, 5-diphenyl-3-pentadienone (IV) (m.p. 109-110°) in 1200 ml of dioxane was prepared in a 2-liter three-necked flask fitted with mechanical stirrer, thermometer, and two dropping funnels. The solution was stirred and cooled with ice water while, over a period of five minutes, 100 ml of 18% hydrogen peroxide and 40 ml of 4 N NaOH were added simultaneously from the dropping funnels. The oxidation reaction was accompanied by slight evolution of heat, and the temperature of the reaction mixture was maintained at not above 20° by cooling. After one hour the whole of the hydrogen peroxide had reacted. The solution was neutralized with 100 ml of 10% sulfuric acid, and the whole was diluted with an equal volume of water. The crystalline precipitate was filtered off, washed on the filter with ethanol, and recrystallized from dioxane. The product, amounting to 95 g, consisted of colorless crystals, m.p. 110-118°.

Repeated fractional crystallization of these crystals from petroleum ether (b.p. 80-100°) gave: a) 18 g of the high-melting isomer of the keto diepoxide (V) in the form of glistening silvery leaves, m.p. 119-119.5°;

Found %: C 76.60; 76.62; H 5.19; 5.28 $C_{17}H_{14}O_3$. Calculated %: C 76.69; H 5.26
Found: M 208; 211 (in benzene) $C_{17}H_{14}O_3$. Calculated: M 266

we were unable to recrystallize the 2, 4-dinitrophenylhydrazone because it resinified when heated in alcoholic solution; and b) 5 g of the low-melting isomer of the keto diepoxide (V) in the form of glistening needles, m.p. 99.5°;

Found %: C 76.31; 76.59; H 5.32; 5.28 $C_{17}H_{14}O_3$. Calculated %: C 76.69; H 5.26

In addition, we obtained an intermediate fraction (70 g, m.p. 86-100°) consisting of a mixture of isomers of the diepoxide (V).

Found %: C 77.11; 77.10; H 5.44; 5.33 $C_{17}H_{14}O_3$. Calculated %: C 76.69; H 5.26

A mixture of the two pure isomers melted at 84-96°.

α-Keto Diepoxide (VII)

Over a period of two hours, 104 g of the dienone (VI) (b.p. 80° (1.5 mm); n_D^{24} 1.5100) [10] and 50 ml of 8 N NaOH were added simultaneously from two dropping funnels to a solution of 250 ml of 24% hydrogen peroxide in 750 ml of dioxane with vigorous stirring and cooling with ice and salt. The oxidation continued for about 5.5 hours and was accompanied by evolution of heat. When reaction was complete, 15 g of hydrogen peroxide remained in the reaction mixture, the excess added being about 13 g. The solution was neutralized with 130 ml of 10% sulfuric acid, hydrogen peroxide was decomposed with manganese dioxide, and the precipitate of sodium sulfate was filtered off. Most of the dioxane was distilled off under reduced pressure (about 100 mm), distillation being continued until the liquid formed two layers.

The product was extracted with ether, and the extract was dried with anhydrous sodium sulfate. Vacuum-fractionation gave 60 g of the diepoxide (VII) in the form of a colorless liquid, b.p. 105-107° (2.5 mm). Repeated chilling of this gave 12 g of the solid isomer of the keto diepoxide (VII), m.p. 54.5° (from petroleum ether).

Found %: C 65.99; 65.83; H 7.93; 7.86 $C_{16}H_{14}O_3$. Calculated %: C 65.93; H 7.89

Repeated fractionation of the liquid fraction gave 35 g of the liquid diepoxide (VII), b.p. 105° (2 mm); n_D^{20} 1.4840; d_4^{20} 1.1281; found MR 46.18; calculated MR 46.48.

Found %: C 65.74; 65.77; H 7.83; 7.81 $C_{16}H_{14}O_3$. Calculated %: C 65.93; H 7.89

Hydrolysis of the Keto Diepoxide (VII)

a) A mixture of 5 g of the keto diepoxide (VII) (m.p. 54.5°) and 100 ml of water was boiled until complete dissolution occurred (15 hours). The solution was evaporated under reduced pressure, and the thick sirupy residue was dissolved in dry chloroform. The solution yielded 3.7 g of crystals of the dihydroxychromanone (VIII), which melted at 81-82° after three recrystallizations from ether.

Found %: C 60.22; 60.19; H 8.17; 8.20 $C_{16}H_{16}O_4$. Calculated %: C 60.00; H 8.00

b) A mixture of 20 g of the keto diepoxide (VII) (b.p. 105-107° (2.5 mm); n_D^{20} 1.4840) and 200 ml of water containing 5 ml of concentrated hydrochloric acid was heated in a boiling water bath for 2.5 hours. When the reaction mixture was cooled, about 5 g of a thick sirup settled on the bottom of the flask. The product was extracted with ether, and the extract was dried with anhydrous sodium sulfate. Vacuum fractionation gave about 13 g of the dihydroxychromanone (VIII) in the form of a thick colorless sirup, b.p. 105-106° (1 mm) and n_D^{20} 1.5060, which gradually congealed into a paste; we did not succeed in crystallizing it.

Keto Epoxide (X)

With continuous stirring, 50 ml of 24% hydrogen peroxide and 15 ml of 4 N NaOH were added to a solution of 45.5 g of the methoxy ketone (IX) (b.p. 100-103° (2 mm); n_D^{20} 1.4880) [10] in 350 ml of methanol cooled to −7° with ice and salt. The oxidation reaction proceeded with slight evolution of heat. After 2.5 hours from the

start of reaction, 4 g of hydrogen peroxide remained in the reaction mixture (the excess added was about 3.5 g). The reaction products were isolated in the usual way. Two vacuum fractionations gave about 30 g of the keto epoxide (X) in the form of a colorless liquid, b.p. 90° (1.5 mm); n_D^{20} 1.4720; d_4^{20} 1.0314; found MR 53.75; calculated MR 53.29.

Found %: C 68.56; 68.71; H 9.41; 9.19 $C_{12}H_{18}O_3$. Calculated %: C 68.87; H 9.09

The high carbon content is probably to be explained by admixture of unchanged methoxy ketone, although reoxidation of the analyzed fraction did not affect the analytical results.

SUMMARY

1. In the oxidation of 1,5-diphenyl-3-pentadienone (IV) and of 1-cyclohexen-1-yl propenyl ketone (VI) with alkaline hydrogen peroxide, in each case two geometric isomers of the corresponding α-keto diepoxide were isolated.

2. It is suggested that the hydrogen peroxide oxidation reaction is accompanied by inversion of the configuration of the original α, β - unsaturated ketone.

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* Original Russian pagination. See C. B. Translation.

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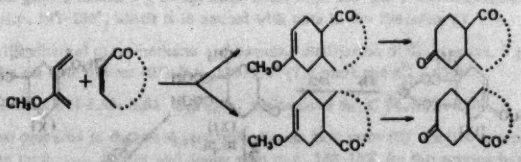
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 15. CONDENSATION OF 2-METHOXY-1, 3-BUTADIENE WITH MALEIC AND CITRACONIC ANHYDRIDES AND WITH THE METHYL ESTERS OF FUMARIC AND MESACONIC ACIDS

I. N. Nazarov and V. F. Kucherov

2-Alkoxy-1, 3-butadienes are notable in that, as a result of diene condensation and hydrolysis of the adducts formed, they can give substituted cyclic ketones, many of which are not readily accessible. As a result, 2-alkoxy-1, 3-butadienes have been used frequently in diene condensations, and the literature contains reports of their reactions with acrolein [1, 2], crotonaldehyde [3], methyl vinyl ketone [3], acrylonitrile [4], maleic and citraconic anhydrides [5], maleic and fumaric esters [7], and p-benzoquinone [8, 9].

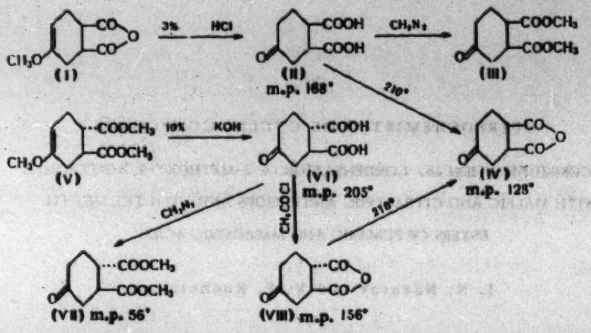
Work in our laboratory [10] has shown that 2-methoxy-1, 3-butadiene is able to condense also with α, β-unsaturated cyclic ketones with formation of the corresponding bicyclic ketones, mainly of para structure:



We considered that it would be of interest to use 2-methoxy-1, 3-butadiene in condensations with anhydrides and esters of some unsaturated cis- and trans-dicarboxylic acids with the object of obtaining stereoisomeric oxo-1, 2-cyclohexanedicarboxylic acids.

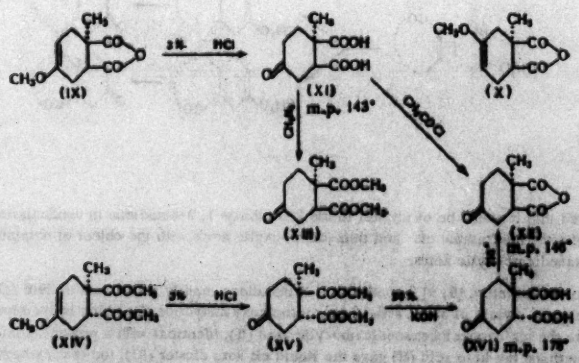
According to the literature [5, 6] 2-methoxy-1, 3-butadiene readily reacts with maleic anhydride; reaction in boiling benzene gives a yield of about 65% of the cis methoxy anhydride (I), which is hydrolyzed by 3% hydrochloric acid into the cis-oxocyclohexanedicarboxylic acid (II), identical with a product obtained previously [11]. With diazomethane the keto acid (II) gave the liquid cis keto diester (III), the semicarbazone of which was found to be different from that obtained by Petrov and Sopov [7]; it melted at 186-187°. Vacuum distillation of the cis keto acid (II) gave the corresponding cis keto anhydride (IV), but when this was obtained by treatment with acetyl chloride at the boil, its formation was accompanied by formation of isomers of lactone character which we did not succeed in isolating in the pure state.

The condensation of 2-methoxy-1, 3-butadiene with methyl fumarate went much better: reaction at 230° for three hours gave the trans methoxy diester (V) [7] in a yield of about 80%. Hydrolysis of the trans methoxy diester (V) with 10% potassium hydroxide solution gave the trans keto acid (VI), m.p. 204-205°, and with diazomethane this gave the trans keto diester (VII), which formed a semicarbazone of m.p. 179-180°.



The melting point of our trans acid (VI) was 15° higher than the value reported in the literature [7]. The trans keto acid (VI), unlike the cis isomer (II), readily gave the trans keto anhydride (VIII) with boiling acetyl chloride. When heated, this anhydride was completely isomerized into the stable cis keto anhydride (IV).

Heating of 2-methoxy-1, 3-butadiene with citraconic anhydride for six hours at 100° gave a good yield of the cis methoxy anhydride (IX), possibly contaminated with a little of the meta isomer (X). However, hydrolysis of the adduct with 3% hydrochloric acid resulted in the isolation of only one individual cis keto acid (XI), m.p. 143°, with a para arrangement of carbonyl and methyl groups, and not meta – the arrangement previously assigned arbitrarily to this compound [8].



The incorrectness of the earlier view was proved by studying the reactions of the cis keto acid (XI) and the condensation of 2-methoxy-1, 3-butadiene with mesaconic ester. It was found that, when boiled with acetyl chloride, the cis keto acid (XI) readily gave the cis keto anhydride (XII), and by the action of diazomethane it gave the cis keto diester (XIII), which was characterized as the semicarbazone, m.p. 182°.

The isomeric trans keto diester (XV), the semicarbazone of which melted at 202°, was prepared by acid hydrolysis of the adduct (XIV) formed in high yield by condensing 2-methoxy-1, 3-butadiene with mesaconic ester (240° for four hours).

Hydrolysis of the trans keto diester (XV) with 20% potassium hydroxide solution also gave only one individual trans keto acid (XVI), m.p. 178°. When heated in a vacuum, this acid was converted in good yield into the isomeric cis keto anhydride (XII), which proved that the isomeric keto acids (XI) and (XVI) are sterically different. The structure of these stereoisomers as 1-methyl-4-oxo-1, 2-cyclohexanedicarboxylic acid follows from the fact that the semicarbazone prepared from the diethyl ester of the trans keto acid (XVI) had the same melting point as that described previously [12] and differed greatly from the known semicarbazone of diethyl trans-1-methyl-5-oxo-1, 2-dicarboxylate [13].

These results show that the condensation of 2-methoxy-1, 3-butadiene with citraconic and mesaconic anhydrides gives mainly adducts of para structure, as in the case of the diene condensations of various 2-substituted dienes with unsymmetrical dienophiles [14].

EXPERIMENTAL

Condensation of 2-Methoxy-1, 3-butadiene with Maleic Anhydride

2-Methoxy-1, 3-butadiene (15 ml) [10] was added to a solution of 20 g of freshly distilled maleic anhydride in 100 ml of dry benzene. The mixture was set aside for two days at room temperature and was then refluxed for five hours. The solution was decanted from the polymer that formed, benzene was distilled off, and the residue was vacuum-distilled. The product, in yield of 24 g (64%), was the cis methoxy anhydride (I), b.p. 130-132° (3 mm) and n_D^{20} 1.5070.

Found %: C 59.59; 59.49; H 5.68; 5.89 $C_9H_{10}O_4$. Calculated %: C 59.34; H 5.53

cis Keto Diester (III). A mixture of 10 g of the cis methoxy anhydride (I) and 30 ml of 3% hydrochloric acid was boiled for 90 minutes and then evaporated to small bulk under reduced pressure. The product gradually crystallized out; it was filtered off and washed with a little cold water (6.2 g, m.p. 160-163°). Evaporation of the aqueous mother liquor gave a further 2 g of the same acid, m.p. 160-162°. Crystallization from water gave pure cis keto acid (II), m.p. 167-168°, which is in accord with data in the literature [7, 11].

After treatment with ethereal diazomethane and vacuum-distillation of the product, 5 g of the cis keto acid (II) gave 4.7 g of the cis keto diester (III), b.p. 130-131° (1.5 mm) and n_D^{20} 1.4740.

Found %: C 56.24; 56.27; H 6.55; 6.51 $C_{10}H_{14}O_5$. Calculated %: C 56.06; H 6.59

The semicarbazone prepared in the usual way from the cis keto ester (III) melted constantly at 186-187° after crystallization from methanol. Petrov and Sopov give m.p. 138-139° for this semicarbazone [7].

Found %: N 15.25; 15.24 $C_{11}H_{19}O_5N_3$. Calculated %: N 15.50

Clemmensen reduction of the cis keto ester (III) gave a good yield of the known cis-1, 2-cyclohexanedicarboxylic acid, m.p. 191-192°, undepressed by admixture of a known sample.

cis Keto Anhydride (IV). The cis keto dicarboxylic acid (II) (2 g) was heated at 210° in a vacuum for 15 minutes and was then distilled at 2 mm. The viscous product (1.3 g) crystallized when treated with benzene, and recrystallization from benzene gave 1.1 g of the cis keto anhydride (IV), which melted constantly at 127-128°.

Found %: C 57.27; 57.09; H 5.17; 5.06 $C_8H_8O_4$. Calculated %: C 57.14; H 4.80

Condensation of 2-Methoxy-1, 3-butadiene with Dimethyl Fumarate

A mixture of 18 g of dimethyl fumarate, 30 g of 2-methoxy-1, 3-butadiene (threefold excess), and 100 ml of dry benzene was heated at 230-235° for three hours. Vacuum fractionation gave 23 g (80%) of the adduct, b.p. 120-125° (2 mm). Redistillation under reduced pressure gave 20.8 g of the trans methoxy diester (V), b.p. 112-113° (1 mm) and n_D^{20} 1.4780, which gradually solidified and then melted at 65-66°, which is in accord with data in the literature [7].

trans Keto Acid (VI). A mixture of 6 g of the trans methoxy diester (V) and 50 ml of 10% potassium hydroxide solution was boiled for 90 minutes until solution was complete. The product was treated with active charcoal, filtered, and acidified with hydrochloric acid. The solution was evaporated under reduced pressure, and the residue was treated with acetone. The acetone solution was evaporated to low bulk, and after several days 2.7 g of the trans keto acid (VI), m.p. 196-198°, separated. After crystallization from a little water the melting point was 204-205°. According to Petrov and Sopov [7], the trans keto acid (VI) melts at 188-190°.

Found %: C 51.83; 51.84; H 5.52; 5.38 $C_9H_{10}O_5$. Calculated %: C 51.81; H 5.41

trans Keto Diester (VII). The trans keto acid (VI) (2.3 g) was treated with diazomethane in ether. Ether was distilled off, and the residue crystallized when treated with petroleum ether. The product (2.3 g) was the trans keto diester (VII), m.p. 53-55°. After being crystallized from a mixture of diethyl ether and the petroleum ether it melted at 55-56°, which is in accord with data in the literature [7]. The semicarbazone, prepared in the usual way, melted at 179-180° after crystallization from methanol. Clemmensen reduction of the trans keto diester (VII) gave the known trans-1, 2-cyclohexanedicarboxylic acid, m.p. 218-220°.

trans Anhydride (VIII). A mixture of 3 g of the trans keto acid (VI) and 25 ml of acetyl chloride was boiled until solution was complete (four hours), and acetyl chloride was then distilled off. The residue gradually crystallized when it was allowed to stand with benzene. The product (1.7 g) was the trans anhydride (VIII), m.p. 151-153°, raised to 155-156° by recrystallization from benzene.

Found %: C 57.12; 57.06; H 4.82; 4.73 $C_9H_8O_4$. Calculated %: C 57.14; H 4.80

Thermal Isomerization of the trans-Keto Acid (VI)

The trans keto acid (VI) (2 g) was heated at 210° for 15 minutes and then vacuum-distilled. Crystallization from benzene gave 1.1 g of the cis keto anhydride (IV), m.p. 125-127°, undepressed by admixture of the sample described above.

Condensation of 2-Methoxy-1, 3-butadiene with Citraconic Anhydride

A mixture of 11 g of citraconic anhydride, 13.2 g of 2-methoxy-1, 3-butadiene, and 50 ml of benzene was heated in a sealed tube at 100° for six hours. Vacuum fractionation gave 14 g of the adduct (IX), b.p. 135-142° (5 mm) and n_D^{20} 1.4930. Redistillation through a column gave 11 g of the cis methoxy anhydride (IX), b.p. 133-135° (3 mm); n_D^{20} 1.4945.

Found %: C 61.38; 61.46; H 6.42; 6.33 $C_{10}H_{12}O_4$. Calculated %: C 61.25; H 6.27

cis-1-Methyl-4-oxo-1, 2-cyclohexanedicarboxylic Acid (XI)

A mixture of 10 g of the cis methoxy anhydride (IX) and 20 ml of 3% hydrochloric acid was boiled for two hours. Water was distilled off under reduced pressure, and the residue was dissolved in benzene. The solution was dried with sodium sulfate, and benzene was distilled off down to low bulk. After several days, 6.5 g of the crystalline cis keto acid (XI), m.p. 132-136°, separated. After crystallization from a mixture of benzene and ether it melted at 142-143°.

Found %: C 53.86; 53.88; H 6.13; 5.97 $C_9H_{12}O_5$. Calculated %: C 53.99; H 6.04

cis Keto Anhydride (XII). A mixture of 0.5 g of the cis keto acid (XI) and 5 ml of acetyl chloride was boiled until solution was complete, and volatile substances were distilled off under reduced pressure. Treatment of the residue with petroleum ether gave 0.3 g of the cis keto anhydride (XII), m.p. 135-140°, which melted constantly at 145-146° after crystallization from benzene.

Found %: C 59.42; 59.10; H 5.80; 5.86 $C_9H_{10}O_4$. Calculated %: C 59.33; H 5.55

cis Keto Diester (XIII). A suspension of 4.5 g of the cis keto acid (XI) in ether was treated with a slight excess of ethereal diazomethane. After removal of ether, the liquid product was vacuum-distilled and gave 5.3 g of the cis keto diester (XIII) as a viscous liquid, b.p. 149-150° (3 mm) and n_D^{20} 1.4730.

Found %: C 57.72; 57.50; H 6.78; 7.03 $C_{11}H_{16}O_5$. Calculated %: C 57.88; H 7.06

After crystallization from methanol the semicarbazone, prepared in the usual way, melted at 162-164°.

Found %: N 14.91; 14.92 $C_{10}H_{19}O_3N_3$. Calculated %: N 14.77

Clemmensen reduction of the cis keto diester (XIII) gave a good yield of cis-1-methyl-1, 2-cyclohexanedicarboxylic acid, m.p. 156-157°, undepressed by admixture of a known sample.

Condensation of 2-Methoxy-1, 3-butadiene with Dimethyl Mesaconate

A solution of 10 g of dimethyl mesaconate and 16 g of 2-methoxy-1, 3-butadiene (a threefold excess) in 30 ml of dry benzene was heated in a steel ampoule at 235-240° for four hours. Benzene was distilled off, and vacuum-distillation of the residue gave 9.9 g of adduct, b.p. 125-135° (4 mm). Redistillation through a column gave 8.9 g of the trans methoxy diester (XIV), b.p. 124-126° (3 mm) and n_D^{22} 1.4780.

Found %: C 59.84; 59.87; H 7.57; 7.70 $C_{10}H_{16}O_5$. Calculated %: C 59.80; H 7.49

trans Keto Diester (XV). A mixture of 6 g of the trans methoxy diester (XIV) and 25 ml of 3% hydrochloric acid was stirred at 40° for three hours, water was distilled off under reduced pressure, the residue was carefully extracted with ether, and the ethereal solution was washed with a little cold water and dried with sodium sulfate. Vacuum distillation gave 4.4 g of the trans keto diester (XV), b.p. 145-146° (3 mm); n_D^{22} 1.4720.

Found %: C 57.87; 57.90; H 7.00; 7.12 $C_{11}H_{16}O_5$. Calculated %: C 57.88; H 7.08

After crystallization from 70% methanol, the semicarbazone prepared from the trans keto diester (XV) melted at 200-201°.

Found %: N 14.53; 14.84 $C_{12}H_{19}O_5N_3$. Calculated %: N 14.77

Clemmensen reduction of the trans keto diester gave pure trans-1-methyl-1, 2-cyclohexanedicarboxylic acid, which showed no depression of melting point in admixture with a known sample.

trans-1-Methyl-4-oxo-1, 2-cyclohexanedicarboxylic Acid (XVI)

A mixture of 3 g of the trans keto diester (XV) and 20 ml of 20% potassium hydroxide solution was boiled for three hours, treated with active charcoal, filtered, and acidified with hydrochloric acid. Water was distilled off under reduced pressure, and the dry residue was carefully extracted with ether. The extract was dried with sodium sulfate, ether was distilled off to low bulk, and the residue was diluted with a little petroleum ether. After several days, 1.15 g of crystals, m.p. 158-165°, formed. On standing, the mother liquor gave a further 0.4 g of crystals, m.p. 150-160°. Two recrystallizations from water gave 1.1 g of the trans keto acid (XVI), m.p. 176-178°.

Found %: C 53.92; 53.88; H 5.96; 5.94 $C_9H_{12}O_5$. Calculated %: C 53.99; H 6.04

Boiling with ethanol in benzene solution in presence of a little sulfuric acid converted the trans keto acid (XVI) into its diethyl ester, b.p. 130-132° (2 mm), semicarbazone m.p. 141-142°, which corresponds to data in the literature [12]. The semicarbazone of the isomeric diethyl trans-1-methyl-5-oxo-1, 2-cyclohexanedicarboxylate melts at 158° [13].

Thermal Isomerization of the trans Keto Acid (XVI)

The trans keto acid (XVI) (0.5 g) was heated under reduced pressure at 210° for 20 minutes. Crystallization from benzene gave 0.3 g of the cis keto anhydride (XII), m.p. 144-145°, undepressed by admixture of the sample obtained previously (above).

SUMMARY

1. A study was made of the condensations of 2-methoxy-1, 3-butadiene with maleic and citraconic anhydrides and with fumaric and mesaconic esters. The corresponding cis- and trans-4-oxo-1, 2-cyclohexanedicarboxylic acids, their anhydrides, and their methyl esters are described.

2. It was shown that, in the condensation of 2-methoxy-1, 3-butadiene with citraconic anhydride and mesaconic ester, mainly para-adducts are formed, and these were characterized by their derivatives.

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MECHANISM OF HYDRATION AND DEHYDRATION REACTIONS IN PRESENCE OF ZINC HALIDES

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Processes of hydration and dehydration are extensively used in the industry of organic synthesis and preparative chemistry for the preparation of substances of great practical importance, particularly alcohols and unsaturated hydrocarbons. These reactions proceed successfully only in presence of catalysts. The catalysts most frequently used are sulfuric and phosphoric acids, alumina, thoria, and various salts [1]. It is to be noted that, in spite of the great practical importance of hydration and dehydration reactions, their mechanisms have not been adequately elucidated. There are various schemes in the literature for the course of these reactions in presence of certain protonic acids [2], but there are substantially no soundly based data on the mechanisms of these reactions in presence of aprotonic acids. We must point out also that metal halides have long been used as hydrating and dehydrating agents; and among these the most extensively used is zinc chloride.

Dehydration of Alcohols

Many investigators [3-5] have studied the dehydration of various alcohols with the aid of zinc chloride, and, on the basis of their experimental results, they have explained the mechanism of the reaction of alcohols with zinc chloride in various ways. Kondakov [6] considers that zinc chloride acts exclusively as a water-eliminating agent and does not admit the possibility of the formation of intermediate compounds. Liebmann [7] also regards zinc chloride as a water-eliminating agent. According to these views, the reaction of zinc chloride with alcohols is expressed in the following scheme:

$$C_nH_{2n+1}OH \xrightarrow{ZnCl_2} C_nH_{2n} + H_2O;$$

$$2C_nH_{2n+1}OH \xrightarrow{ZnCl_2} (C_nH_{2n+1})_2O + H_2O.$$

Other authors, however, hold a different view of the mechanism of reactions of zinc chloride with alcohols. Thus, going back to Williamson [8], we find that in his theory of the formation of ethers he considered that zinc chloride reacts like sulfuric acid with alcohols, forming intermediate zinc alkoxides, which then give ethers:

$$2C_2H_5OH + ZnCl_2 = (C_2H_5O)_2Zn + 2HCl;$$

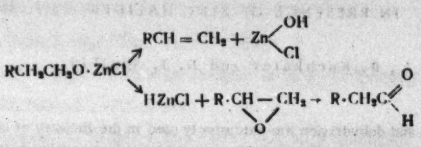
$$2C_2H_5OH + 2HCl = 2C_2H_5Cl + 2H_2O;$$

$$(C_2H_5O)_2Zn + 2C_2H_5Cl = 2C_2H_5 \cdot O \cdot C_2H_5 + ZnCl_2.$$

The same view was developed later by Walter [9], who observed the formation of mixed zinc alkoxides in the reaction of zinc chloride with alcohols:

$$i\text{-}C_5H_{11}OH + ZnCl_2 \rightarrow i\text{-}C_5H_{11}OZnCl + HCl.$$

At high temperature the mixed zinc alkoxide decomposed into various new substances:



From the products of this reaction Walter succeeded in isolating an oily compound, to which he ascribed the formula $C_5H_{11}OZnCl$, although there was a great discrepancy between the found and calculated values for the zinc, carbon, and hydrogen contents. After an investigation of the decomposition products of aluminum and zinc alkoxides, Tishchenko [10] concluded that reaction between alcohols and zinc chloride proceeds as follows:

$$ZnCl_2 + 2ROH \rightarrow Zn(OR)_2 + 2HCl;$$

$$2ROH + 2HCl \rightarrow 2RCl + 2H_2O.$$

The author considered that the alkyl chloride reacts with the zinc alkoxide with formation of an ether,

$$Zn(OR)_2 + 2RCl \rightarrow ZnCl_2 + 2R_2O.$$

and olefins are formed by decomposition of the zinc alkoxide. Favorsky [11] pointed out the resemblance between the mechanisms of the reactions of sulfuric acid and zinc chloride with α-glycols and assumed the formation of mixed zinc alkoxides as intermediate products.

There is, therefore, a divergence of opinion on the mechanism of the dehydration of alcohols in presence of zinc chloride, and it is difficult to judge which of the suggested schemes is the correct one. The views of authors of the first group, which assume that zinc chloride is merely a water-removing agent, are not in accord with the experimental facts and, in our opinion, must be regarded as doubtful. The various schemes proposed by authors of the other group, which assume the formation of intermediate compounds in the course of the dehydration of alcohols under the action of zinc chloride, have the drawback of being based on indirect experimental facts. For example, when reaction between zinc chloride and alcohols was carried out at high temperatures (350-400°) in iron vessels [3, 4], there were by-products in the formation of which iron and its oxide probably played a major part. However, in the establishment of the mechanism of the action of zinc chloride on alcohols the effect of these factors was not taken into consideration by earlier investigators.

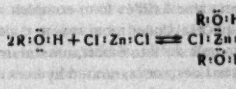
With the object of elucidating the nature of the catalytic effect of zinc halides in the course of hydration and dehydration, we undertook an investigation of the reactions of alcohols and olefins with zinc chloride and bromide [12]. Taking into account the importance of studying intermediate products for the establishment of reaction mechanisms, we first tried to determine the conditions for the formation of the products which, as we showed, are formed in the reaction between zinc halides and alcohols. We studied the action of anhydrous zinc

chloride and bromide on methyl, ethyl, propyl, isopropyl, butyl, isobutyl, isopentyl, benzyl, cyclohexyl, and other alcohols. Experiments were carried out in glass apparatus with various proportions of reactants under various conditions of temperature. After prolonged trials, we succeeded in isolating complex compounds of zinc chloride and bromide with alcohols. It was found that in these complexes zinc chloride and bromide are combined with alcohols in various proportions, which depend on reaction conditions and the identity of the alcohol. Compounds of zinc chloride and bromide of composition $ZnX_2 \cdot ROH$ and $ZnX_2 \cdot 2ROH$ were obtained, and sometimes compounds of other compositions were formed [13]. For example, study of the fusion diagram of the system zinc chloride–cyclohexanol confirmed the formation of the compound $ZnCl_2 \cdot 2C_6H_{11}OH$. These complexes are viscous oily liquids that are heavier than water. They are very hygroscopic and readily liquefy in the air. They are readily soluble in many organic solvents (benzene, toluene, acetone, alcohol, ether), but are almost insoluble in petroleum ether. Their solutions have acid properties and are electrically conducting. Thus, the molecular conductivity of zinc chloride in absolute methanol at 75° was found [14] to be 2.88 at 2.778 moles/liter, 1.49 at 4.884 moles/liter, and 0.560 at 5.84 moles/liter.

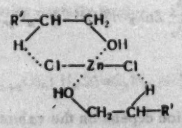
A study of the pH of aqueous and alcoholic solutions of zinc chloride and some other metal halides showed [15] that change in the concentration of the halide has a great effect on pH. It should be noted that, in solutions of $ZnCl_2$ and $CaCl_2$ in absolute ethanol, the quinhydrone electrode did not show a salt error. This indicates that these salts interact completely with the alcohol with formation of complex compounds. Benzene solutions of the crystalline complexes formed by zinc chloride and bromide with cyclohexanol, 2-methyl-2-butanol, tert-butyl alcohol, and some other alcohols show acid reactions to various indicators (4-phenylazo-1-naphthylamine, Methyl orange, Dimethyl yellow, litmus).

The acid properties of zinc chloride and bromide complexes are shown clearly also in their effects on alkylation, acylation, esterification, and addition reactions, which generally go very well in presence of acid catalysts (H_2SO_4, H_3PO_4, HF, etc.). Thus, good yields of carboxylic esters and acetals are obtained in presence of zinc halide complexes [16]. According to Meerwein, the acid properties of concentrated aqueous zinc chloride solutions are to be explained by the formation of complex compounds which have the properties of acids. The author measured the acidity of concentrated aqueous zinc chloride solutions by their catalytic activity on the inversion of sugar [17].

Thus, all these facts confirm the view that the appearance of acid functions in alcoholic solutions of zinc halides is due to the formation of complex acids. It is probable that complex-formation between zinc halides and alcohols proceeds by interaction between the electron-acceptor zinc ion and the electron-donor oxygen atom of the alcoholic hydroxyl:



In our opinion, the possibility that the complex has a cyclic structure cannot be excluded:



The possibility of the formation of such cyclic intermediate complexes in the course of reaction was pointed out by Shilov [18] in explaining the mechanism of addition to unsaturated molecules.

In alcoholic solutions of zinc chloride, the latter does not dissociate into chloride and zinc ions [19]. The electrical conductivity of these solutions must be attributed to hydrogen ions from the alcoholic hydroxyl. This is in accord with the fact that the alcohols themselves, particularly the lower ones, have acidic, although very weakly acidic, properties. Methanol, for example, has an ionization constant of 10^{-16}. It is clear that the formation of new bonds with the oxygen atom will weaken the bond between the oxygen and hydrogen of the hydroxy group, so that the complexes formed will behave like the usual mineral acids:

$$2ROH + ZnCl_2 \rightleftarrows H_2\left[\begin{matrix} RO \\ RO \end{matrix}\!\!>\!ZnCl_2\right] \rightleftarrows 2H^+ + \left[\begin{matrix} RO \\ RO \end{matrix}\!\!>\!ZnCl_2\right]$$

We also studied the behavior of these complexes toward heat. We found that, unlike the compounds formed by $CaCl_2$, $MgCl_2$, and $CdCl_2$ with alcohols, the molecular compounds of zinc halides, depending on the nature of the complexed alcohol and the temperature of treatment, break down with formation of various new compounds. For example, when methanol and ethanol complexes of zinc chloride are heated at 200-230°, gaseous and liquid products are formed. The gaseous decomposition products from the methanol complex were found to contain 10-12% of unsaturated hydrocarbons. The liquid products consisted mainly of dimethyl ether and the original alcohol; no aldehydes or other compounds were detected.

The decomposition of the ethanol complex began at 170° with formation of diethyl ether, the original alcohol, and gases containing 90% of ethylene. No aldehydes, hydrogen, or saturated hydrocarbons were detected among the decomposition products. In the breakdown of complexes of propyl alcohol (decomposition temperature 200°), butyl alcohol (decomposition temperature 185°), isopropyl alcohol (decomposition temperature 160°), and hexyl alcohol (decomposition temperature 170°), mainly unsaturated hydrocarbons, their polymers, and small amounts of the original alcohol and water were formed. Aldehydes, hydrogen, and saturated compounds were again absent in the decomposition products.

When heated to 140-145°, the crystalline complex of cyclohexanol and zinc chloride decomposed into cyclohexene (85% yield), cyclohexene dimer, high-boiling products, and water. Zinc bromide complexes gave similar results. It should be noted that slow dropwise addition of various alcohols to zinc chloride heated to 300° in a hard-glass flask results in the formation of products similar to those obtained by the decomposition of zinc halide complexes.

Hence, at relatively low temperatures, zinc halides form complex compounds of acidic character with alcohols, their general formula being $ZnX_2 \cdot nROH$. Under more severe conditions of temperature complex-formation is accompanied by decomposition of the complexes into ethers, unsaturated hydrocarbons, the original alcohols, and water. No aldehydes, hydrogen, alkyl halides, or saturated hydrocarbons are formed.

Hence, the reaction of dehydration of alcohols in presence of zinc halides can be represented as the formation in the first place of an intermediate compound ($ZnX_2 \cdot nROH$), which then, depending on the identity of the alcohol and the conditions of heating, decomposes with formation of various substances. The course of the reaction can be represented as follows:

$$ZnX_2 + nROH \underset{k_2}{\overset{k_1}{\rightleftarrows}} ZnX_2 \cdot n\,ROH \xrightarrow{k_3} C_nH_{2n},\ ROR,\ H_2O$$

and other products.

The final results of the dehydration reaction depend on the values of the rate constants k_1, k_2, and k_3.

It should be noted that, according to some authors [20], at first ethers are formed and, under given reaction conditions, these then decompose in presence of catalysts into olefins. On the other hand, other investigators [21] consider that ethers are not intermediaries in the formation of olefins.

The results of our investigations on the dehydration of alcohols with the aid of zinc halides show that olefins can arise both directly in the decomposition of intermediate complexes, and also as a result of the breakdown of ethers formed in the course of the dehydration. For example, the dehydration of lower alcohols (CH_3OH, C_2H_5OH) with $ZnCl_2$ and $ZnBr_2$ is accompanied by simultaneous formation of ethers and olefins. Moreover, in the dehydration of alcohols of higher molecular weight we were unable to isolate any appreciable amount of the corresponding ethers from the reaction products: the ethylenic hydrocarbons were almost always formed in quantitative yield. Similar results were obtained also in the thermal decomposition of the individual zinc halide complexes. For example, when heated above their melting points, the crystalline complex compounds of $ZnCl_2$ and $ZnBr_2$ with tertiary alcohols (tert-butyl alcohol, 2-methyl-2-butanol) decomposed quantitatively into the corresponding olefins.

The formation of ethers in the dehydration of alcohols depends mainly on the nature of the latter. Generally speaking, ethers are obtained in good yield only in the dehydration of lower alcohols. The reaction probably goes as follows:

$$CH_3OH + ZnCl_2 \rightleftarrows [ZnCl_2 \cdot OCH_3]\,H \rightleftarrows [ZnCl_2 \cdot OCH_3]^- + \overset{+}{H}.$$

Alcohols, being amphoteric compounds, can ionize as acids or as bases. In an acid medium they behave as bases, i.e., give carbonium and hydroxyl ions:

$$CH_3OH \rightleftarrows \overset{+}{CH_3} + \overline{OH}$$

$$\overset{+}{H} + \overline{OH} \rightleftarrows H_2O.$$

The carbonium ion then reacts with the anion of the acidic complex with formation of a new intermediate compound which then decomposes with formation of an ether:

$$[ZnCl_2 \cdot OCH_3]^- + \overset{+}{CH_3} \rightleftarrows [ZnCl_2 \cdot OCH_3]\,CH_3$$
$$[ZnCl_2 \cdot OCH_3]\,CH_3 + HOH \rightarrow CH_3OCH_3 + ZnCl_2 \cdot H_2O.$$

This scheme explains to some extent why reaction with lower alcohols (methanol, ethanol) proceeds with a comparatively high yield of ether. This is probably to be explained by the fact that in the case of methanol and ethanol we are dealing with the most active alcohols, which dissociate more strongly than their higher homologs. In the case of the higher alcohols their complexes decompose under certain temperature conditions directly into the corresponding unsaturated hydrocarbons and hydroxohalozinc acids:

$$ZnX_2 + n\,C_nH_{2n+1}OH \rightleftarrows [ZnX_2 \cdot (C_nH_{2n+1}O)_n]\,H_n.$$

in which n is the number of alcohol molecules (usually two):

$$[ZnX_2(C_nH_{2n+1}O)_n].H_n \rightleftarrows nC_nH_{2n} + [ZnX_2 \cdot (OH)_n]\,H_n.$$

Thus, the dehydration of 2-methyl-2-butanol in presence of zinc chloride proceeds as follows:

$$ZnCl_2 + 2C_5H_{11}OH \rightleftarrows [ZnCl_2 \cdot (C_5H_{11}O)_2]\ H_2 \rightleftarrows$$
$$\rightleftarrows 2C_5H_{10} + [ZnCl_2 \cdot (OH)_2]\ H_2$$
$$\downarrow\uparrow$$
$$ZnCl_2 + 2H_2O.$$

As will be seen from this scheme, as pentene and water are removed from the sphere of reaction, equilibrium is moved to the right, and zinc chloride enters into reaction with the alcohol.

It is probable, therefore, that acidic complexes between zinc halides and alcohols play the same part in the dehydration reaction that alkyl hydrogen sulfates play in dehydration with sulfuric acid, forming, like alkyl hydrogen sulfates, ethers under some conditions and unsaturated hydrocarbons under others.

Hydration of Olefins

We must point out that there are contradictory views on the mechanism of addition of water to unsaturated hydrocarbons in presence of zinc halides as catalysts. In the opinion of some investigators [22], in the hydration reaction zinc halides activate the double bonds of unsaturated compounds. According to the results of other investigations [23], hydration proceeds under the action of hydrohalic acid formed by the hydrolysis of zinc halide.

In order to determine the part played by zinc halides in the hydration reaction, we first studied the possibility of the formation of intermediate complexes between olefins and zinc halides. Kondakov [22] unexpectedly discovered molecular compounds of pentenes with $ZnCl_2$. For this purpose he used pure $ZnCl_2$ and various pentene isomers obtained from fermentation amyl alcohol. On the basis of his analyses he attributed the composition $C_5H_{10} \cdot 2ZnCl_2$ to the compound. Kondakov noted that, in the reaction between moist 2-methyl-2-butene and $ZnCl_2$, the formation of the crystalline product was accelerated. However, he did not admit the possibility of the participation of water in the composition of these substances; he considered that water simply played the part of solvent.

In our opinion, it is here impossible to neglect the fact that zinc chloride reacts more vigorously with water than with unsaturated hydrocarbons. As is well known, zinc chloride combines with water with evolution of a considerable amount of heat, whereas we have found that well dried unsaturated hydrocarbons do not react with anhydrous $ZnCl_2$. For example, we left a mixture of dry 2-methyl-2-butene and anhydrous zinc bromide in sealed tubes for several months, and no addition products were formed. It is evident that, when water is present in the reaction medium, zinc chloride will in the first place react with the water.

Hence, it is very probable that water participates directly as a reactant in complex-formation between ethylenic hydrocarbons and zinc halides. We succeeded in isolating crystalline complexes of zinc chloride and bromide with various unsaturated hydrocarbons, using moist olefins of zinc halides for this purpose. The following compounds were isolated:

$$C_5H_{10} \cdot 2ZnCl_2 \cdot H_2O,\ C_5H_{10} \cdot 2ZnBr_2 \cdot H_2O \text{ and } (C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O.$$

The last of these complexes was prepared by reaction of dry 2-methyl-2-butene with previously prepared zinc bromide hydrate $ZnBr_2 \cdot 2H_2O$.

Hence, the formation of complexes of unsaturated hydrocarbons with zinc halides depends on the presence of a definite amount of moisture in the reaction medium. Our observations confirm Meerwein's suggestion about the existence of hydroxochlorozinc acids of general formula $[(ZnCl_2) \cdot nH_2O]$ [17]. Thus, unsaturated hydrocarbons react not with anhydrous zinc halides, but with various hydroxochloro- and hydroxobromo-zinc acids with formation of hygroscopic crystalline complexes. Investigation of the properties of these compounds showed that they are acidic in character: their solutions in absolute benzene show an acidic reaction to 4-phenylazo-1-naphthylamine. When treated with water, these compounds decompose into the corresponding alcohols and hydroxochloro- or hydroxobromo-zinc acids.

It was further established that the product obtained by reaction of zinc bromide with 2-methyl-2-butanol was identical, both in composition and in properties, to the substance obtained from the hydroxobromozinc acid

$[ZnBr_2 \cdot (OH)_2]H_2$ and 2-methyl-2-butene. The two preparations had the same melting point (63°) and had acidic properties. When treated with water they both gave 2-methyl-2-butanol. This crystalline substance, therefore, is the intermediate complex common to the reactions of hydration of 2-methyl-2-butene and the dehydration of 2-methyl-2-butanol. In its general form, the reaction can be represented by the scheme:

$$[ZnBr_2 \cdot (OH)_2]H_2 + 2C_nH_{2n} \rightleftharpoons [ZnBr_2 (C_nH_{2n+1}O)_2]H_2 \rightleftharpoons 2C_nH_{2n+1}OH + ZnBr_2.$$

As will be seen from this scheme, an equilibrium exists between the hydration and dehydration reactions. Depending on the conditions, equilibrium is displaced either in the direction of dehydration of the alcohol or in the direction of hydration of the olefin.

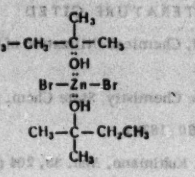
Hence, the hydration of 2-methyl-2-butene in presence of a zinc halide proceeds according to the scheme:

$$ZnBr_2 + 2H_2O \rightleftharpoons [ZnBr_2(OH)_2]H_2 \quad (1)$$

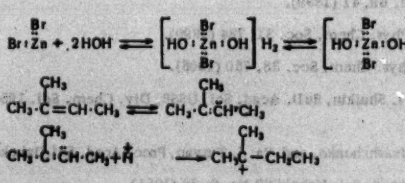
$$[ZnBr_2 \cdot (OH)_2]H_2 + 2C_5H_{10} \rightleftharpoons [ZnBr_2 \cdot (OH)_2]H_2 \cdot 2C_5H_{10}. \quad (2)$$

$$[ZnBr_2 \cdot (OH)_2]H_2 \cdot 2C_5H_{10} \xrightarrow{2HOH} 2C_5H_{11}OH + [ZnBr_2 \cdot (OH)_2]H_2. \quad (3)$$

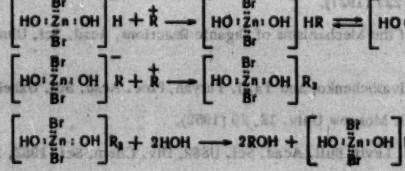
It is possible that addition of the hydroxobromozinc acid to 2-methyl-2-butene gives the following complex:



Thus, the hydration of unsaturated hydrocarbons in presence of zinc halides proceeds in two stages. In the first stage hydroxohalozinc acids add to unsaturated hydrocarbons, the process being analogous to the addition of mineral acids. In the second stage, on addition of water, the addition compounds decompose like alkyl hydrogen sulfates with formation of the corresponding alcohols and hydroxo acids. From the point of view of electronic theory, the reaction can be represented as follows:



If we denote $(CH_3)_2\overset{+}{C} \cdot CH_2 \cdot CH_3$ by $\overset{+}{R}$, then



SUMMARY

1. It is shown that, in the hydration of olefins and dehydration of alcohols in presence of zinc halides as catalysts, intermediate complexes are formed which later decompose, in a manner dependent on conditions, with formation of the final reaction products.

2. Both in the reaction of zinc halides with alcohols and in the reaction between hydroxchalozinc acids and the unsaturated hydrocarbons corresponding to these alcohols, the same intermediate complexes are formed. This indicates the existence of a state of equilibrium between the reactions of hydration of olefins and dehydration of alcohols. On the basis of these data and of a detailed investigation of the composition of complexes formed by zinc halides with alcohols and unsaturated hydrocarbons, a possible mechanism is proposed for hydration and dehydration reactions in presence of zinc halides as catalysts.

3. Comparison between hydration and dehydration reactions catalyzed by zinc halides, on the one hand, and by mineral acids, on the other, shows that they are very similar in mechanism.

4. On the basis of theoretical considerations and of a study of the properties of the intermidiate zinc halide compounds, a possible structure is proposed for the intermediate complexes.

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OXIDATION-REDUCTION SYSTEMS FOR THE INITIATION OF FREE-RADICAL PROCESSES

COMMUNICATION 1. REVERSIBLE SYSTEMS IN WHICH ORGANIC HYDROPEROXIDES, DIENOLS, AND SALTS OF METALS OF VARIABLE VALENCE TAKE PART

G. P. Belonovskaya, B. A. Dolgoplosk, and E. I. Tinyakova

Oxidation-reduction systems have recently received considerable application for the initiation of free-radical processes, particularly polymerization processes in aqueous emulsions. The present investigation is devoted to a study of the mechanism of the action of reversible oxidation-reduction systems consisting of organic hydroperoxides, traces of iron or copper salts, and dienols (dihydroxymaleic and ascorbic acids) that are well known as components of natural biochemical oxidation-reduction systems. The systems that we developed were found to be extremely effective for the initiation of polymerization in aqueous emulsions.

Mechanism of the Action of the System

In order to determine by what mechanism the system acts and the parts played by individual reactions in the initiation of the polymerization process, it was considered to be necessary to study the kinetics of the interaction of the components in media of water and aqueous emulsions.

a) Kinetics of the Reactions of Dihydroxymaleic and Ascorbic Acids with Cumene Hydroperoxide. The kinetics of the reactions were studied in aqueous solutions in an atmosphere of nitrogen completely freed from oxygen; the concentrations of oxidizing and reducing agents were equimolecular and were about 0.15%. The kinetics of the process were characterized by following the changes in the contents of hydroperoxide (b) and dienol (a) in the reaction mixture. In a study of the effect of pH on the rate of reaction of cumene hydroperoxide with dihydroxymaleic acid it was shown that a minimum rate is found when reaction occurs at a pH of about 7; lowering or raising of pH leads to increased rate of reaction. In the case of ascorbic acid, reaction proceeds most slowly in acid and neutral media. The results of the experiments are shown in Figures 1-5.

In absence of metal salts, reaction between dihydroxymaleic or ascorbic acid and the hydroperoxide in an acid medium proceeds comparatively slowly (Curve 1, Figures 1 and 2) and scarcely goes at all at -15° and at -35° (Curve 1, Fig. 3). At pH 10.5 reaction between the hydroperoxide and ascorbic acid proceeds at an appreciable rate even in absence of iron or copper salts (Curve 1, Fig. 4). Even in this case, lowering of temperature to -15° and -35° leads to the complete cessation of the process (Fig. 5).

In all pH regions, reaction between the components is considerably accelerated by the introduction of salts of metals of variable valence into the system in very low concentration. In an acid medium iron salts are the more effective, and in an alkaline medium copper salts have the greater effect. As Figures 1-5 show, by varying the concentration of the metal salt we may regulate reaction rate over a wide range. Thus, at pH 3 (created by the dihydroxymaleic acid itself) and 0°, reaction is greatly accelerated by the introduction of only 0.5 mole % of Mohr's salt, (based on the amount of the hydroperoxide) (Curve 2, Fig. 1); in presence of 10 mole % of Mohr's salt, dihydroxymaleic acid almost disappears from the system in 15 minutes (Curve 3, Fig. 1). The case of ascorbic acid (Fig. 2) is similar, but metal salts are effective in considerably lower concentrations than in the dihydroxymaleic acid system.

The accelerating effect of metal salts is particularly notable at -15° and -35°, i.e., under the conditions under which cumene hydroperoxide scarcely reacts at all with dienols; with lowering of temperature the effective concentration of metal salt increases. The same situation is found also with dihydroxymaleic acid in an alkaline

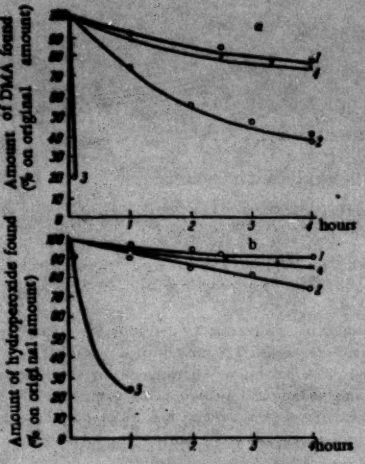


Fig. 1. Kinetics of reaction of dihydroxymaleic acid (DMA) with cumene hydroperoxide as function of concentration of metal salt at 0° and pH 3: 1) no metal salt added; 2) Mohr's salt 0.5 mole % on hydroperoxide; 3) Mohr's salt 10 moles % on hydroperoxide; 4) $CuSO_4 \cdot 5H_2O$ 0.7 mole % on hydroperoxide.

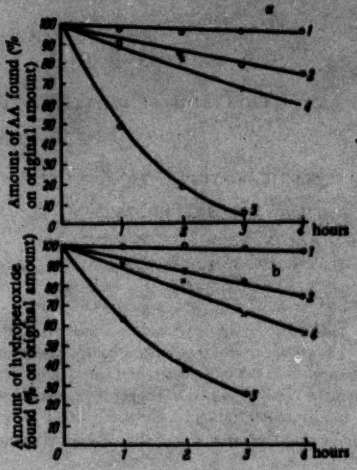
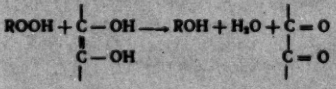


Fig. 2. Kinetics of reaction of ascorbic acid (AA) with cumene hydroperoxide as function of concentration of metal salt at 0° and pH 3: 1) no metal salt added; 2) Mohr's salt 0.1 mole % on hydroperoxide; 3) Mohr's salt 0.5 mole % on hydroperoxide; 4) $CuSO_4 \cdot 5H_2O$ 0.7 mole % on hydroperoxide.

medium at -15° (Fig. 5). For the attainment of the necessary reaction rate, the concentration of copper salt must be raised to 0.2-0.4% on the amount of hydroperoxide.

The kinetics of the consumption of the hydroperoxide are almost always closely similar to those of the consumption of dienol, which is in accord with the overall equation:



However, since the products of the oxidation of dienols have fairly high reducing properties in alkaline media, their participation in reactions with metal salts and with the hydroperoxide results in departures from this stoichiometrical relation (Fig. 4). That such departures are likely to occur follows also from the complex character of the reaction, with participation of free radicals in the intermediate stages.

b) Reactions of Cumene Hydroperoxide and Dihydroxymaleic Acid with Iron Salts. In order to determine the kinetics of the oxidation of Fe^{2+} into Fe^{3+} by cumene hydroperoxide, solutions of the hydroperoxide and of Mohr's salt were cooled to 0° and mixed. Test samples were taken immediately and after five minutes, and these were analyzed for unchanged ferrous iron and for the sum of ferric iron and hydroperoxide. For the study of the reduction of Fe^{3+} into Fe^{2+} by dihydroxymaleic acid, equivalent amounts of ferric ammonium alum and

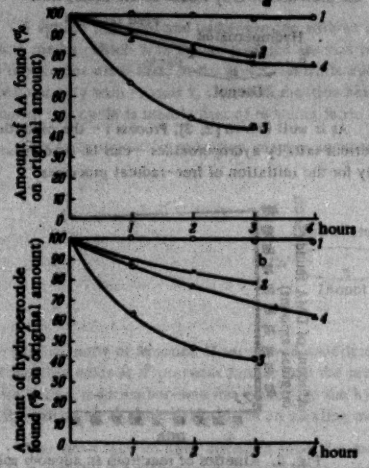


Fig. 3. Kinetics of reaction of ascorbic acid (AA) with cumene hydroperoxide in presence of iron salts in an acid medium (pH 3) at -15° and -35°: 1) no metal salt added (-15° and -35°); 2) Mohr's salt 0.2 mole % on hydroperoxide at -15°; 3) Mohr's salt 0.4 mole % on hydroperoxide at -15°; 4) Mohr's salt 2.0 moles % on hydroperoxide at -35°.

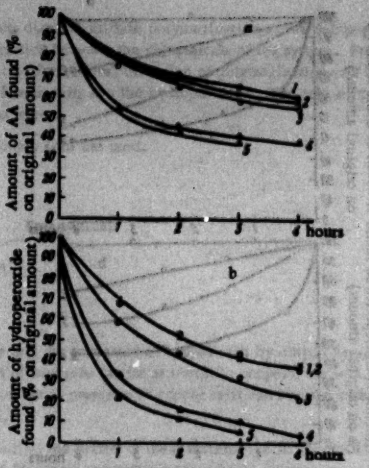


Fig. 4. Kinetics of reaction of ascorbic acid (AA) with cumene hydroperoxide in an alkaline medium (pH 10.5) in presence of iron salts at 0°: 1) no metal salt added; 2) Mohr's salt 0.1 mole % on hydroperoxide; 3) Mohr's salt 0.5 mole % on hydroperoxide; 4) $CuSO_4 \cdot 5H_2O$ 0.5 mole % on hydroperoxide; $CuSO_4 \cdot 5H_2O$ 0.7 mole % on hydroperoxide.

dihydroxymaleic acid were separately dissolved in 0.1 N HCl at 0° and mixed. Test samples were taken immediately and after 5 and 10 minutes, and these were analyzed for unchanged dihydroxymaleic acid and ferric iron. Fig. 6 represents graphically the reactions between cumene hydroperoxide and ferrous salts (Curve 2), between dihydroxymaleic acid and a ferric salt (Curve 3), and between the hydroperoxide and dihydroxymaleic acid (Curve 1).

Comparison of the curves in Fig. 6 shows that oxidation and reduction of iron salts by the hydroperoxide and by dihydroxymaleic acid (Curves 2 and 3) proceed almost instantaneously at 0°. However, direct reaction between the hydroperoxide and dihydroxymaleic acid is very slow. Hence, in this system, ferric salts are considerably more vigorous oxidizing agents than the hydroperoxide. It is known that the reduction of ferric iron by ascorbic acid is instantaneous [1]. It must be stated also that at 0° the ferric salts that are formed have no direct effect on the decomposition of the hydroperoxide; this reaction proceeds at an appreciable rate only above 50°.

c) Mechanism of the Action of the System in the Polymerization Process. The results obtained in our study of the kinetics of individual reactions permit us to arrive at a conclusion about the mechanism of action of the oxidation-reduction system taken as a whole. When the hydroperoxide, dienol, and salt of a metal of variable valence are present simultaneously, the leading role is taken by processes that are very fast, i.e., the alternating reactions of reduction of Fe^{3+} by the dienol and oxidation of Fe^{2+} by the hydroperoxide. In the system consisting of the hydroperoxide, hydroxymaleic (or ascorbic) acid, and an iron salt, a reversible cycle of

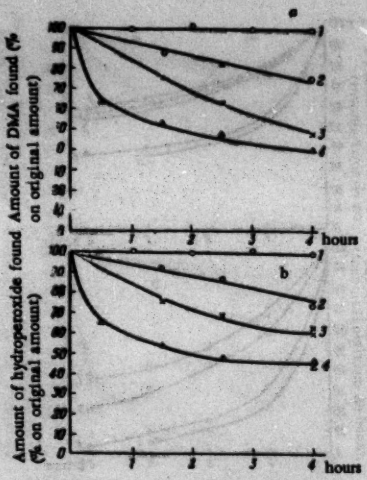
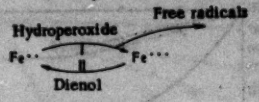


Fig. 5. Kinetics of reaction of dihydroxymaleic acid (DMA) with cumene hydroperoxide in an alkaline medium (pH 11) at ~15°: 1) no metal salt added; 2) $CuSO_4 \cdot 5H_2O$ 0.2 mole % on hydroperoxide; 3) $CuSO_4 \cdot 5H_2O$ 0.4 mole % on hydroperoxide; 4) $CuSO_4 \cdot 5H_2O$ 0.8 mole % on hydroperoxide.

transformations arises, the operation of which is ensured by the presence of only traces of the metal salt.



As is well known [2, 3], Process I – the oxidation of ferrous salts by hydroperoxides – can be used effectively for the initiation of free-radical processes.

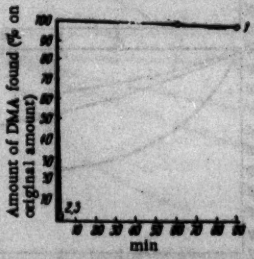
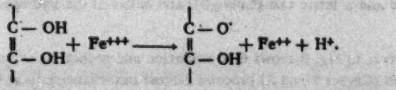
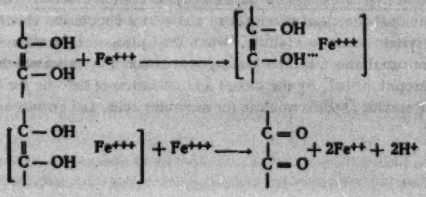


Fig. 6. Kinetics of reactions in aqueous solutions at 0° in an acid medium: 1) cumene hydroperoxide + dihydroxymaleic acid; 2) cumene hydroperoxide + Fe^{2+}; 3) dihydroxymaleic acid + Fe^{2+}.

Process II – the reduction of ferric iron by dienols in aqueous solution – cannot be used for the initiation of polymerization, which indicates that the reaction is more complex than could be foreseen from the bimolecular scheme



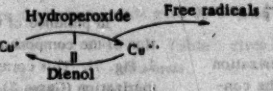
If we take account of the tendency of dienols to form complex compounds with heavy-metal salts, the reaction can be represented as follows, without intermediate free-radical stages:



As one of us and Kropacheva [4] showed, in those cases in which the reducing agent for the ferric salts is a substance that does not form complexes with ferric iron, the reduction of Fe^{3+} to Fe^{3+} can be used for the initiation of polymerization.

A system of dienol and hydroperoxide without iron salts does not initiate polymerization at low temperature in acid media, which is in accord with the absence of interaction between the components of the system. From this it becomes clear that, in the given reversible cycle of transformations, initiation of polymerization can be associated only with Process I, i.e., with reaction between ferrous salts and the hydroperoxide. The role of the dienol in this cycle is merely that of reducing ferric salts to ferrous.

The same oxidation-reduction changes occur when copper salts are used.



In our study of Reaction II we showed experimentally that the reduction of copper salts by dihydroxymaleic and ascorbic acids at 0° proceeds further than the reduction of iron salts (as far as metallic copper). As will be shown below, reaction between the dienol and the hydroperoxide in presence of copper salts can be used effectively for the initiation of polymerization in an alkaline medium.

The views that we have discussed about the mechanism of the action of these systems are in accord with the fact, which we have established, of the impossibility of forming a reversible system based on stannous salts, which are readily oxidized by the hydroperoxide into the stannic form, but cannot be regenerated, under the conditions studied, by reduction with the dienol.

The systems studied are very close to biochemical systems in composition. The establishment of the possibility of the initiation of free-radical processes with the aid of these systems is an indirect confirmation of earlier suggestions by various authors [5] concerning the probable development of biochemical oxidation-reduction processes through a free-radical stage.

Initiation of Polymerization in an Aqueous Emulsion

In aqueous emulsions, one component of the system (the hydroperoxide) is in the hydrocarbon phase, and and the other two (the dienol and the metal salt) are in the aqueous phase. The reaction between the hydroperoxide and the ferrous salt, which proceeds at the interface, determines the general kinetics of the process. In a water-hydrocarbon emulsion reaction is considerably slower than in a homogeneous aqueous medium, and this creates the necessary conditions for the application of the reaction for the initiation of polymerization.

In full accord with our results on the kinetics of reactions between the components in aqueous solutions, a system consisting of the hydroperoxide and the dienol without metal salt does not initiate polymerization below 0°. For example, in presence of the binary system of ascorbic acid and cumene hydroperoxide in an acid medium at -15° (sodium di-tert-butylnaphthalenesulfonate being used as emulsifier), no polymerization occurs. Addition of Mohr's salt in a concentration of 0.02 mole % on the amount of hydroperoxide results in effective initiation of the polymerization process. By varying the concentration of metal salt we may vary the rate of reaction between the components of the system and the related rate of polymerization.

It should be noted that, as might be expected, the system containing ascorbic acid is effective for polymerization in presence of much lower amounts of iron salt than those required in the dihydroxymaleic acid system. For example, the polymerization of butadiene at -15° in presence of the ascorbic acid system proceeds effectively when the concentration of Mohr's salt is 0.02 mole % on the hydroperoxide (50% yield of polymer in 16.5 hours), whereas under the same conditions in presence of the dihydroxymaleic acid system and 0.82 mole % of Mohr's salt a yield of 60% is attained only after 40 hours.

It is an important fact that increase in the content of metal salt above a certain value can lead not to acceleration of the polymerization process, but to retardation and, in certain cases, complete inhibition. The

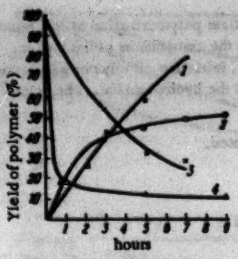


Fig. 7. Kinetics of the polymerization of butadiene (1 and 2) and of the consumption of ascorbic acid (3 and 4): 1 and 3) Mohr's salt 0.02 mole % on hydroperoxide; 2 and 4) Mohr's salt 0.07 mole % on hydroperoxide.

retardation of polymerization with increase in the iron concentration above a certain limit is associated with rapid consumption of components of the system. Here, probably, lies the source of the inhibiting action, noted by many investigators, of salts of copper and other metals for the initiation of polymerization by peroxides.

The effect of iron concentration on the relation between the kinetics of polymerization and the interaction of the components of the system is seen clearly in Fig. 7, which relates to the polymerization of butadiene in an acid medium.

In presence of 0.02 mole % of Mohr's salt the consumption of the components proceeds in a uniform manner (Curve 1, Fig. 7). This corresponds to a uniform process of polymerization (Curve 3). Increase in the concentration of Mohr's salt to 0.07 mole % affects the kinetics of both processes substantially (Curves 2 and 4). Polymerization, which is very fast at first, then comes almost to a stop (Curve 2), this behavior being associated with the rapid consumption of components of the oxidation-reduction system, as can be seen from Curve 4.

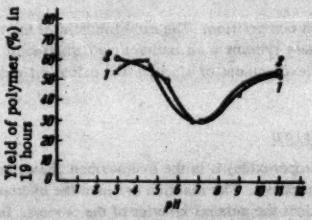


Fig. 8. Kinetics of the polymerization of a mixture of butadiene and styrene in an emulsion (1) and kinetics of the decomposition of dihydroxymaleic acid in its reaction with the hydroperoxide in an aqueous medium (2) as functions of the pH of the medium at 0°.

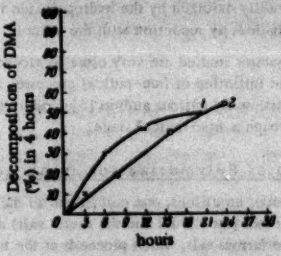


Fig. 9. Kinetics of the polymerization of a mixture of butadiene and styrene in an alkaline medium in presence of a system containing dihydroxymaleic acid and a copper salt: 1) 5°, $CuSO_4 \cdot 5H_2O$ 0.2 mole % on hydroperoxide; 2) 15°, $CuSO_4 \cdot 5H_2O$ 0.5 mole % on hydroperoxide.

The direct connection between the kinetics of the interaction of the components of the system in aqueous solutions and the kinetics of polymerization in emulsions is shown quite clearly by a study of the effect of the pH of the medium on the polymerization process. As is shown in Fig. 8, the curve for the rate of emulsion polymerization as a function of the pH of the medium has the same character as the curve for the rate of interaction of the components of the system in aqueous solutions and passes through a minimum in the neutral range (Fig. 8).

In an alkaline medium, as would be expected from the kinetics of the interaction of components of the system, emulsion polymerization proceeds most efficiently in presence of very small amounts of copper salts (Fig. 9). Taking this case as our example, we have shown that copper salts, which were previously regarded as inhibitors of polymerization processes, may act in certain concentrations as extremely effective activators for these processes.

EXPERIMENTAL

a) Determination of the Dienols and the Hydroperoxide. Dihydroxymaleic and ascorbic acids were determined by titration with 0.1 N iodine in presence of starch. The applicability of this method was previously checked for media of water and aqueous emulsions. Cumene hydroperoxide was also determined iodometrically. For the determination of the hydroperoxide in dilute aqueous solutions containing 0.1-0.15% of the hydroperoxide, the following analytical procedure was adopted: 2 g of crystalline potassium iodide and 5 ml of 60% sulfuric acid were added to 30-40 ml of the aqueous solution of cumene hydroperoxide. The flask was closed with a ground-in stopper moistened with potassium iodide solution, and the contents were carefully mixed until the potassium iodide had dissolved completely. The mixture was set aside in the dark for one hour, and the iodine liberated was titrated with 0.05 N thiosulfate solution in presence of starch. When cumene hydroperoxide and dihydroxymaleic or ascorbic acid were both present in the solution, the dienol was first determined in a sample by titration with iodine, and then the cumene hydroperoxide was determined. The dienol was thus determined almost quantitatively, and the titration for the hydroperoxide gave 96-97% of the true value.

TABLE 1

Determination of Cumene Hydroperoxide and Dihydroxymaleic Acid when Simultaneously Present in Aqueous Solutions

No.	Amount introduced		Amount found (%)	
	Dihydroxymaleic acid	Cumene hydroperoxide	Dihydroxymaleic acid	Cumene hydroperoxide
1	0.0410	—	99.4	—
2	—	0.0400	—	99.5
3	0.0430	0.0400	100.4	96.5
4	0.0430	0.0400	99.5	96.0
5	0.0500	0.0450	100.8	97.3

Table 1 gives the results of analyses of artificial mixtures.

b) Determination of Ferrous and Ferric Salts in Presence of the Hydroperoxide and Dienol. In our study of the oxidation of Fe^{2+} into Fe^{3+} by cumene hydroperoxide, the Fe^{2+} concentration was determined by titration with 0.1 N $K_2Cr_2O_7$ and the sum of the amounts of Fe^{3+} formed and unused hydroperoxide was determined by reaction with HI and subsequent titration with 0.1 N thiosulfate. The results given in Table 2 show that the iodometric method gives adequate accuracy both in the determination of each of the components separately and in the determination of the overall content of hydroperoxide $+Fe^{3+}$

In presence of dihydroxymaleic acid and its decomposition products ferric iron cannot be determined by the usual iodometric method. In a study of the kinetics of the reduction of Fe^{3+} to Fe^{2+} by dihydroxymaleic acid, ferric iron has been determined by titration with 0.1 N $K_4Fe(CN)_6$ [6]. This method enables us to determine ferric iron in presence of dihydroxymaleic acid and gives values of 97-99% of the true value. The content of dihydroxymaleic acid was determined by titration with iodine in 0.1 N HCl. Under these conditions Fe^{2+} is not oxidized by iodine.

TABLE 2

Verification of the Procedure for the Simultaneous Determination of Hydroperoxide and Ferric Iron in Artificial Mixtures

No.	Amount introduced into mixture (g)		Amount found (%)	
	Hydroperoxide	Fe^{+++} (ferric ammonium alum)	Hydroperoxide	Fe^{+++}
1	—	0.0426	—	99.3
2	—	0.0400	—	98.5
3	0.0548	—	99.2	—
4	0.0650	—	100.2	—
5	0.0300	0.0250	100.7	Total content of Fe^{+++} + hydroperoxide
6	0.0300	0.0250	99.5	
7	0.0300	0.0250	100.1	

c) Experimental Procedure. The kinetics of the interaction of the components of the system were studied in aqueous solutions for equimolecular proportions of hydroperoxide and dienol at concentrations of about 0.15%. A solution of the hydroperoxide in water or in aqueous glycerol was introduced into the vessel, which was blown out with nitrogen and cooled to the temperature of the experiment. Dihydroxymaleic or ascorbic acid, dissolved in the minimum amount of water, was then introduced into the vessel, and a test sample was taken for the determination of hydroperoxide and dienol concentrations. When reaction was carried out in presence of a metal salt, this was introduced into the apparatus as an aqueous solution. The experiments were carried out at 0°, -15°, and -35°. The temperature of the thermostat was maintained constant within ± 0.5°.

SUMMARY

1. A study was made of the mechanism of the action of reversible oxidation-reduction systems consisting of an organic hydroperoxide, a dienol, and an iron or copper salt.

2. It was shown that it is possible to use these systems for the initiation of polymerization at low temperatures.

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CHLOROMETHYLATION OF TOLUENE

I. N. Nazarov and A. V. Semenovsky

Chloromethylation of toluene has recently attracted attention as a possible basis for the preparation of terephthalic acid, a raw material for the manufacture of the synthetic fiber Terylene. Unlike the chloromethylation of benzene, which has been studied in detail [1], the chloromethylation of toluene has not received adequate attention in the literature, and on the question of the direction of the reaction, i.e., the relative amounts of the isomers formed, the data are very contradictory. Thus, in 1920 in work on chloro- and bromo-methylation with the aid of bishalomethyl ethers, Stephen and others [2] found that the entry of chloro- and bromo-methyl groups into monosubstituted benzenes occurs exclusively in the para-position.

In 1923, Blanc [3], who developed the well known method of chloromethylation with paraform and hydrogen chloride, reported that toluene gives the para-isomer. Later, papers [4-7] appeared which indicate the formation of a mixture of ortho- and para-isomers in the chloromethylation of toluene, but only in one of these [6] was the composition of the mixture of α-chloroxylenes (here obtained both by Stephen's method and by Blanc's method) determined.

The relative amounts of isomers were determined by thermal analysis of the mixture of alcohols obtained by hydrolysis of the mixture of α-chloroxylenes. It was found that the mixture prepared by Stephen's method contained 53.2% of the ortho-isomer, and the mixture prepared by Blanc's method contained 41.7% of the ortho-isomer. Nevertheless, a paper appeared in 1951 [8] which reported that Blanc chloromethylation of toluene gives α-chloro-p-xylene. In 1953 there appeared a report [9] of the formation of a mixture of 64% para-, 34.7% ortho-, and 1.3% meta-isomer by the chloromethylation of toluene in acetic acid. In the same year it was reported [10] that the content of para-isomer can be raised to 80% by chloromethylation in concentrated hydrochloric acid in absence of catalyst. Finally, after we had completed the present investigation, there appeared a paper [11] in which it was shown viscosimetrically that a mixture of α-chloro-o- and α-chloro-p-xylenes is formed in approximately equal proportions in the chloromethylation of toluene.

The present investigation on the chloromethylation of toluene is concerned mainly with orientation. We considered two of the various methods of chloromethylating toluene: 1) the method, already used for benzene, of treatment with paraform and hydrogen chloride in presence of anhydrous zinc chloride in excess of the hydrocarbon as solvent; and 2) treatment with paraform or formaldehyde in concentrated hydrochloric acid in absence of zinc chloride.

As a result of many experiments on the chloromethylation of toluene by the first method we found that the best result (71.5% yield) is attained by carrying out the reaction under the conditions recommended by Lock [12] for the chloromethylation of benzene, but with a smaller amount of catalyst (zinc chloride). Increase in the amount of zinc chloride without change in the other conditions leads to increase in the yield of ditolylmethane (see table).

Addition of anhydrous aluminum chloride to the zinc chloride also results in greater amounts of ditolylmethane and resinous residue. Addition of thionyl chloride results in almost complete absence of α-chloroxylenes and the formation of much ditolylmethane (49.1%) and products of higher molecular weight. A similar result is obtained when zinc chloride is completely replaced by thionyl chloride.

Addition of various amounts of phosphorus trichloride and phosphoric oxide again did not result in increased yield of α-chloroxylenes. Apart from the amount and composition of the catalyst, the temperature of the reaction

TABLE

Amount of $ZnCl_2$ (g) for 200 g of toluene and 15 g (0.5 mole) of paraform	7.5	8.5	10.0	13.0
Amount of ditolylmethane (g)	7.8	9.6	12.5	24.9

mixture and the duration and efficiency of stirring greatly affect the chloromethylation process. Rise in temperature and increase in the duration of reaction resulted in an increase in the amount of by-products formed. Use of carbon tetrachloride instead of toluene as solvent did not lead to increased yield of the desired product. It follows from these considerations that a reduction in the amount of by-products may be expected if the chloromethylation reaction is carried out in absence of zinc chloride and other catalysts that can promote Friedel-Crafts side reactions. We therefore studied the chloromethylation of toluene in concentrated hydrochloric acid, in absence of zinc chloride. When the reaction was carried out under the recommended conditions, i.e., passage of hydrogen chloride for 25 hours through a vigorously stirred mixture of toluene, paraform, and concentrated hydrochloric acid at 55°, the product of the chloromethylation of toluene was obtained in 70.5% yield without an appreciable amount of by-products. It was found that the 25-hour passage of hydrogen chloride is unnecessary for the success of the process, a passage of 1.5-2 hours, for the more rapid depolymerization of the paraform and raising of the hydrochloric acid concentration, being adequate. The yield of chloromethylation product was then 56.4% on the amount of toluene taken and 71.3% on the amount that reacted. In all cases the chloromethylation product was a liquid distilling at 92-94° (21 mm) which could not be resolved by fractionation through a 15-plate column.

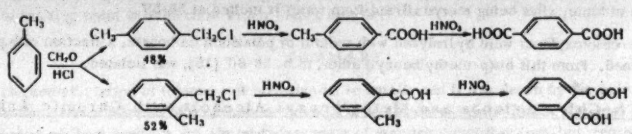
The main purpose of the present investigation was the determination of the composition of the mixture of isomeric α-chloroxylenes obtained by the chloromethylation of toluene. The presence of a mixture of isomeric α-chloroxylenes in the product of the chloromethylation of toluene was indicated immediately by various facts. For example, by oxidation of the chloromethylation product with chromic anhydride in acetic acid, only terephthalic acid in a yield of only 41.2% was obtained, for under these conditions chromic anhydride oxidizes the ortho-isomer completely with rupture of the benzene ring. Hydrolysis of the chloromethylation product does not give the crystalline p-methylbenzyl alcohol (m.p. 58-59°), but a liquid mixture of isomeric methylbenzyl alcohols, from which only by freezing could the para-isomer of m.p. 58-59° be isolated (yield about 30%).

The quantitative determination of the proportions of the isomeric α-chloroxylenes in the products of the chloromethylation of toluene was carried out by comparing the amount of terephthalic acid formed by chromic anhydride oxidation of pure p-methylbenzyl alcohol with the amount formed similarly from the mixture of methylbenzyl alcohols obtained by hydrolysis of the chloromethylation product of toluene. Thus, by the oxidation of pure p-methylbenzyl alcohol, terephthalic acid is obtained in 81.2% yield, and in the oxidation under strictly analogous conditions of the mixture of methylbenzyl alcohols obtained by hydrolysis of the chloromethylation product of toluene (or in the oxidation of the actual chloromethylation products), the yield of terephthalic acid is only 39.2%. It follows from these results that chloromethylation of toluene gives a mixture of α-chloroxylenes containing 48.3% of the para-isomer and 51.7% of the ortho-isomer. Isophthalic acid, which corresponds to the meta-isomer, was not detected in any of the experiments.

Similar results were obtained by oxidation of the mixture of methylbenzyl alcohols obtained after freezing out a definite amount of the para-isomer (48.6% of para- and 51.4% of ortho-isomer). These calculations are based on the well known experimental fact—which we have verified—that in oxidation with chromic anhydride only the para- and meta-isomers give the corresponding benzenedicarboxylic acids (terephthalic and isophthalic acids) in good yield (80-85%), whereas the ortho-isomer is completely broken down in this oxidation and does not give phthalic acid. A series of experiments on oxidation with different excesses of chromic anhydride gave agreeing results. Our results are in close accord with results on the mixture of α-chloroxylenes obtained by the physical methods of thermal analysis (53.2% of ortho-isomer) [6] and viscometry (about 50% of ortho-isomer) [11].

With the object of directly determining the ortho-isomer in the chloromethylation products of toluene, the mixture of α-chloroxylenes was oxidized to benzenedicarboxylic acids with dilute nitric acid at 200° [13]. The total yield of dicarboxylic acids was 81%, from which phthalic acid was isolated in 32% yield and terephthalic acid in 49% yield.

Unlike chromic anhydride, dilute nitric acid oxidizes also the ortho-isomer at high temperatures (about 200°), with fairly smooth formation of phthalic acid:



Oxidation of the mixture of α-chloroxylenes with boiling dilute nitric acid gave the corresponding mixture of toluic acids, from which, by crystallization of the calcium salts [14], o- and p-toluic acids were isolated. Oxidation of the resulting mixture of toluic acids with chromic anhydride gave terephthalic acid in an amount corresponding to the content of para-isomer in the original mixture of α-chloroxylenes (about 48%).

The method that we used for establishing the proportions of isomers obtained in the chloromethylation of toluene makes it possible rapidly to obtain results on the composition of the mixture, for, having once made a comparative oxidation with the pure para-isomer, in further work we need only determine the yield of terephthalic acid obtained directly by oxidation of the mixture of α-chloroxylenes. It was thus shown that in the chloromethylation of toluene by paraform or formaldehyde in a medium of concentrated hydrochloric acid, and also in presence of a catalyst, the same mixture of α-chloroxylenes – 48% of para- and 52% of ortho-isomer – is always obtained. An attempt was made to alter the proportions of the isomers in favor of the para-isomer. With this object toluene was chloromethylated in presence of other catalysts, such as $AlCl_3$, $SnCl_4$, $SiCl_4$, H_2SO_4. It was found that replacement of zinc chloride in this way does not affect the relative amounts of isomers to any practical extent, while at the same time it lowers the yield of α-chloroxylenes (to about 40% for $SnCl_4$ and $SiCl_4$, and still lower in the other cases). This result agrees with conclusions arrived at in a recent paper [11].

EXPERIMENTAL

Chloromethylation of Toluene in presence of Zinc Chloride in Excess of the Hydrocarbon

A mixture of 200 g of toluene, 15 g (0.5 mole) of paraform, and 8.5 g of anhydrous zinc chloride was prepared in a three-necked flask fitted with reflux condenser, thermometer, tube for passage of gas, and an efficient stirrer. A rapid stream of hydrogen chloride was passed for 20 minutes through the vigorously stirred mixture; the reaction temperature rose to 50°. After the passage of hydrogen chloride, the mixture was stirred for one hour at 50°. The toluene layer was then washed carefully: first with water, then with sodium bicarbonate solution, and again with water. The solution was dried with calcium chloride, and toluene was distilled off. The mixture of α-chloro-o- and α-chloro-p-xylenes, amounting to 50 g (71.5%), boiled at 78-80° (10 mm). In addition, 9.6 g of ditolylmethanes, b.p. 140-145° (7 mm), was obtained.

Chloromethylation of Toluene in Concentrated Hydrochloric Acid in absence of Zinc Chloride

Hydrogen chloride was passed for 25 hours into a vigorously stirred mixture of 138 g of toluene, 58.5 g of paraform, and 180 ml of concentrated hydrochloric acid at 55°. The organic layer was carefully washed with water and sodium bicarbonate solution, and was dried over calcium chloride. Fractionation gave a little unchanged toluene and 148.7 g of a mixture of α-chloro-o- and α-chloro-p-xylenes, b.p. 96-97° (26 mm). The yield was 70.5% on the amount of toluene that reacted.

Hydrolysis of a Mixture of α-Chloro-o- and α-Chloro-p-xylenes

The above-described mixture of α-chloroxylenes (30 g), water (100 ml), and chalk (15 g) were introduced into a three-necked flask fitted with reflux condenser and stirrer. The contents of the flask were stirred vigorously and boiled for 25 hours. The resulting mixture of methylbenzyl alcohols was extracted with dichloroethane and dried over potassium carbonate. Vacuum distillation of the product gave 19.7 g (77%) of a mixture of o- and p-methylbenzyl alcohols, b.p. 120-122°(24 mm). By repeated freezing, 5.4 g of pure p-methylbenzyl alcohol was isolated from this mixture; after being recrystallized from water it melted at 58-59°.

When the α-chloroxylenes were hydrolyzed with sodium or potassium carbonate, a fraction of b.p. 170-173° (5 mm) was obtained. From this bis(p-methylbenzyl) ether, m.p. 58-60° [15], was isolated.

Oxidation of α-Chloroxylenes and Methylbenzyl Alcohols with Chromic Anhydride

a) A mixture of 4.1 g of the above-described mixture of α-chloro-o- and α-chloro-p-xylenes, 30 g of chromic anhydride, 90 ml of water, 90 ml of acetic acid, and 30 ml of sulfuric acid was refluxed until exothermic oxidation set in. When spontaneous heating ceased, the reaction mixture was boiled further for one hour. After cooling, filtration, and drying of the crystals that separated, 2 g (41%) of terephthalic acid was obtained; its dimethyl ester melted at 141-142°, and in admixture with a known sample there was no depression of melting point.

Other oxidation experiments were carried out under strictly identical conditions, and the following results were obtained:

b) By oxidation of 3.56 g of pure p-methylbenzyl alcohol, m.p. 58-59°, 3.93 g (81.2%) of terephthalic acid was obtained.

c) By oxidation of 3.56 g of the mixture of methylbenzyl alcohols corresponding to the original mixture of α-chloroxylenes, 1.90 g (39.2%) of terephthalic acid was obtained.

d) By oxidation of 3.56 g of the mixture of methylbenzyl alcohols remaining after the pure para-isomer had been frozen out, 1.11 g (22.9%) of terephthalic acid was obtained.

e) By oxidation of 3.97 g of the mixture of toluic acids obtained by oxidation of the original mixture of α-chloroxylenes with dilute nitric acid (see below), 1.90 g (39.2%) of terephthalic acid was obtained.

In all these experiments the terephthalic acid obtained was identified by its dimethyl ester, m.p. 141-142°, undepressed by admixture of a known sample.

Esterification of Terephthalic Acid

A mixture of 1 g of terephthalic acid, 15 ml of methanol, and 1.5 g of concentrated sulfuric acid was refluxed for ten hours. The crystals that precipitated on cooling were filtered off and recrystallized from methanol. The product, amounting to 1 g (91%), was dimethyl terephthalate, m.p. 141-142°, undepressed by admixture of a known sample.

Oxidation of the Mixture of α-Chloroxylenes with Dilute Nitric Acid at 200°

A mixture of 3.5 g of the α-chloroxylene mixture and 84 ml of 10% nitric acid was introduced into a 200-ml rotating autoclave. Agitation was continued for 90 minutes at 200°. The autoclave was cooled, and 2.02 g of water-insoluble terephthalic acid was isolated and identified as its dimethyl ester, m.p. 141-142°. Evaporation of the mother liquor and recrystallization of the residue from 5% hydrochloric acid gave 1.3 g of phthalic acid, the anilide of which melted at 209-210° and showed no depression of melting point in admixture with a known sample. The total yield of acids was 3.32 g (81%).

Oxidation of the Mixture of α-Chloroxylenes to Toluic Acids

The mixture of α-chloroxylenes (50 g) was refluxed with 1700 ml of 5% nitric acid for 50 hours. The crystals of toluic acids which precipitated on cooling were filtered off, recrystallized from water, and dried in a desiccator. The yield was 37.1 g (76.6%).

The mixture of toluic acids was separated with the aid of their calcium salts, which were obtained by the action of calcium hydroxide. When boiled with water, the calcium salt of o-toluic acid passed into solution and the calcium salt of p-toluic acid remained and was filtered off. The filtrate was evaporated to dryness and the residue was crystallized twice from alcohol, thus giving the calcium salt of o-toluic acid. The calcium salts obtained were treated with dilute hydrochloric acid, and the free toluic acids were recrystallized from water and dried in a vacuum desiccator. In this way, from 5 g of the above-described mixture of toluic acids, 0.5 g of pure o-toluic acid, m.p. 102-103°, and 0.9 g of p-toluic acid, m.p. 179-180°, were isolated. Neither showed depression of melting point in admixture with a known sample.

SUMMARY

The chloromethylation of toluene was investigated in detail, and it was shown by the oxidation method that the reaction gives a mixture of α-chloro-o-xylene and α-chloro-p-xylene in almost equal proportions. The relative amounts of these products are almost independent of reaction conditions (catalyst, temperature, solvent, etc.).

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* C. r. = Compt. rend.

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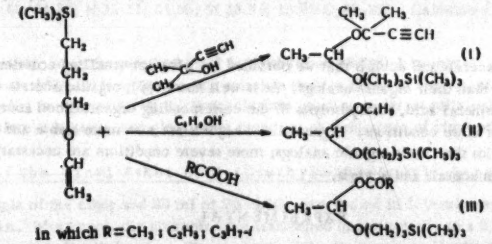
SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

COMMUNICATION 3. SYNTHESIS AND SOME REACTIONS OF VINYL ETHERS OF 3-(TRIMETHYLSILYL)- AND 3-(DIETHYLMETHYLSILYL)-1-PROPANOL

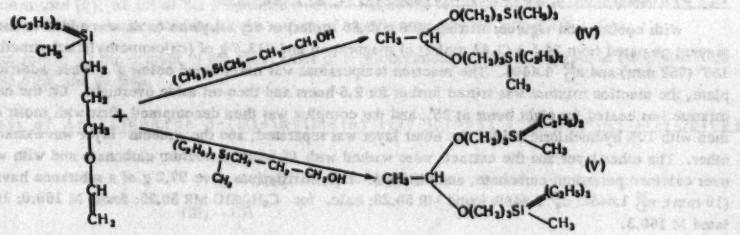
M. F. Shostakovsky, I. A. Shikhiev, and N. V. Komarov

Vinyl ethers of organic [1] and organosilicon [2] alcohols are of great theoretical and practical interest at the present time. In previous investigations we synthesized 3-(trimethylsilyl)-1-propanol [2] and carried out some of its reactions [3]. We showed also that reaction of vinyl ethers with silanols [4] and organosilicon alcohols [5] gave the corresponding organosilicon acetals, whereas reaction with organic acids [1] gave partial acylals.

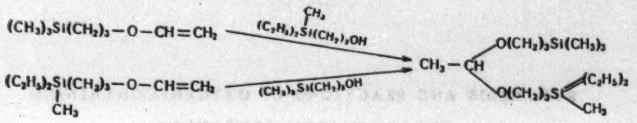
With the object of studying the reactivities and proving the structures of the vinyl ethers of organosilicon alcohols that we have prepared, in the present investigation we have converted them into organosilicon acetals and acylals and made a comparative study of the properties of these derivatives. The reactions proceeded as follows:



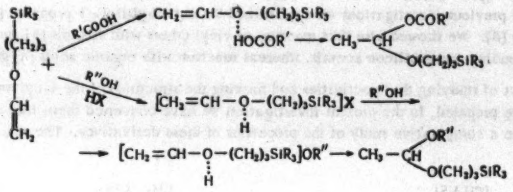
in which R = CH_3; C_2H_5; C_3H_7-i



The structure of one of the acetals (IV) was proved by its synthesis by two different methods:



It should be noted that the chemistry and reactivities of organosilicon acetals have not been discussed in the literature, and there is no information at all about organosilicon acylals. We consider that the mechanism of the formation of organosilicon acetals and acylals from vinyl ethers of organosilicon alcohols and organic alcohols and acids is analogous to that of the formation of the corresponding organic acetals and acylals [1] and can be represented as follows:



The organosilicon acetals and acylals that we obtained are pleasant-smelling colorless liquids, insoluble in water and more stable than their organic analogs. As is well known [6], organic acetals are readily hydrolyzed in presence of traces of mineral acid, but hydrolysis of the corresponding organosilicon acetals proceeds only to the extent of 5-12% under these conditions. Organosilicon acylals are also more stable and more difficultly hydrolyzable by mineral acids than their organic analogs; more severe conditions are necessary for the complete hydrolysis of organosilicon acetals and acylals.

EXPERIMENTAL

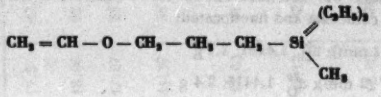
1. Synthesis of 3-(Diethylmethylsilyl)-1-propanol

With cooling and vigorous stirring, 126 g (2.85 moles) of dry ethylene oxide was added to the Grignard reagent prepared from 34.5 g (1.42 moles) of magnesium and 213.5 g of (chloromethyl)diethylmethylsilane, b.p. 155° (752 mm) and n_D^{20} 1.4405. The reaction temperature was maintained below 9°. When addition was complete, the reaction mixture was stirred further for 2.5 hours and then set aside overnight. On the next day the mixture was heated for eight hours at 35°, and the complex was then decomposed, first with moist ether, and then with 10% hydrochloric acid. The ether layer was separated, and the aqueous layer was extracted twice with ether. The ether layer and the extracts were washed with 1% aqueous sodium carbonate and with water, dried over calcined potassium carbonate, and distilled. Two distillations gave 97.2 g of a substance having b.p. 98° (10 mm); n_D^{20} 1.4452; d_4^{20} 0.8489; found MR 50.28; calc. for $C_9H_{20}SiO$ MR 50.35; found M 169.0; 164.8; calculated M 160.3.

Found %: C 60.24; 60.18; H 12.52; 12.74; Si 18.29 $C_9H_{20}SiO$. Calculated %: C 59.94; H 12.57; Si 17.5

These results correspond to 3-(diethylmethylsilyl)-1-propanol. The average yield in a series of experiments was 42%.

2. Synthesis of the Vinyl Ether of 3-(Diethylmethylsilyl)-1-propanol



A 500-ml rotating steel autoclave was loaded with 3-(diethylmethylsilyl)-1-propanol (55 g) and 7.5% potassium ethoxide solution (1.054 g of potassium). The air in the autoclave was displaced by acetylene, and the autoclave was then filled with acetylene at a pressure of 18 atm and was heated for five hours at 170-180°. The autoclave was cooled to room temperature, and a second portion of acetylene was introduced, this operation being repeated until acetylene ceased to be absorbed. The contents of the autoclave—64.5 g of a dark-brown liquid of pleasant ethereal odor—were transferred to a Favorsky flask, distilled under reduced pressure, and treated with sodium to remove unchanged alcohol. Fractionation of the product gave the following fractions:

Fraction I. b.p. 75-83° (9 mm); 4.8 g; n_D^{20} 1.4385

Fraction II. b.p. 83-85° (9 mm); 28.3 g; n_D^{20} 1.4415

Fraction III. b.p. 85-88° (9 mm); 14.7 g; n_D^{20} 1.4420

Residue in still 2.1 g

Fractions II and III were combined, treated with sodium, and distilled. The product amounted to 41.5 g and had b.p. 82-83° (8 mm); n_D^{20} 1.4415; d_4^{20} 0.8326; found MR 59.80; calc. for $C_{10}H_{22}SiO$ MR 59.36.

Found %: C 64.05; 64.20; H 12.11; 11.95; Si 15.80; 15.98 $C_{10}H_{22}SiO$. Calculated %: C 64.45; H 11.00 Si 15.06

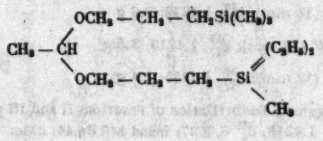
These results correspond to the vinyl ether of 3-(diethylmethylsilyl)-1-propanol. The average yield in a series of experiments was 68%. This substance is a colorless mobile liquid of very pleasant odor, insoluble in water, but readily soluble in organic solvents. It decolorizes bromine water, readily polymerizes in presence of traces of 5% ferric chloride solution, and gives other reactions characteristic of vinyl ethers, which are being studied.

3. Hydrolysis of the Vinyl Ether of 3-(Diethylmethylsilyl)-1-propanol

A weighed sample of the ether and 20 ml of 2% H_2SO_4 were sealed in 150-ml tube and heated in a boiling water bath for six hours. When cool, the contents were transferred quantitatively to a 200-ml measuring flask and made up to volume with distilled water. The contents of the flask were well mixed, and the acetaldehyde content was determined [6]: 15 ml of 0.1 N bisulfite solution was added to 50 ml of the solution under test, the mixture was well stirred, and after 15 minutes the excess of bisulfite was titrated with 0.1 N iodine.

Triplicate results for the content of the vinyl ether of 3-(diethylmethylsilyl)-1-propanol in our preparation were 96.21%, 95.80%, and 95.85%.

4. Synthesis of Acetaldehyde 3-(Diethylmethylsilyl)propyl 3-(Trimethylsilyl)propyl Acetal



Concentrated hydrochloric acid (0.02 ml) was added to a vigorously stirred mixture of 7.45 g (0.04 mole) of the vinyl ether of 3-(diethylmethylsilyl)-1-propanol (b.p. 82-83° (8 mm); n_D^{20} 1.4415) and 5.28 g (0.04 mole) of 3-(trimethylsilyl)-1-propanol (b.p. 79-80° (24 mm); n_D^{20} 1.4296) at 18°. The temperature of the reaction mixture rose to 53°, and the mixture was then heated at 65° for 30 minutes. It was set aside overnight, and was then neutralized with potassium carbonate and fractionated:

Fraction I. b.p. 50-100° (2 mm); n_D^{20} 1.4401; 1.1 g

Fraction II. b.p. 101-131° (2 mm); n_D^{20} 1.4418; 2.4 g

Fraction III. b.p. 132-133° (2 mm); n_D^{20} 1.4429; 7.36 g

Residue in still, b.p. 133° (2 mm); 1.5 g

Redistillation of Fractions II and III gave 8.65 g (69%) of a substance of b.p. 131-132° (2 mm); n_D^{20} 1.4428; d_4^{20} 0.8582; found MR 98.39; calc. for $C_{16}H_{36}Si_2O_2$ MR 99.01.

Found %: C 59.93; 59.87; H 11.93; 12.04; Si 17.37; 17.00 $C_{16}H_{36}Si_2O_2$. Calculated %: C 60.30; H 12.02; Si 17.63

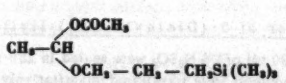
These results correspond to acetaldehyde 3-(diethylmethylsilyl)propyl 3-(trimethylsilyl)propyl acetal.

5. Synthesis of Acetaldehyde 3-(Diethylmethylsilyl)propyl 3-(trimethylsilyl)propyl Acetal

Reaction under similar conditions between 6.32 g (0.04 mole) of the vinyl ether of 3-(trimethylsilyl)-1-propanol (b.p. 61° (18 mm); n_D^{20} 1.4265) and 6.40 g (0.04 mole) of 3-(diethylmethylsilyl)-1-propanol (b.p. 98-99° (10 mm); n_D^{20} 1.4430) gave 7.95 g (62.5%) of a substance having b.p. 140-141° (3 mm); n_D^{20} 1.4425; d_4^{20} 0.8589; found MR 98.26; calc. for $C_{16}H_{36}Si_2O_2$ MR 99.01. In physicochemical constants this substance is identical with the 3-(diethylmethylsilyl)propyl 3-(trimethylsilyl)propyl acetal obtained in the previous experiment by another route.

The other organisilicon acetals (Tables 1 and 2) were prepared under similar conditions by the same procedure.

6. Synthesis of Acetic Ester of 1-[3-(Trimethylsilyl)propoxy]ethanol



A mixture of 4.95 g (0.03 mole) of the vinyl ether of 3-(trimethylsilyl)-1-propanol (b.p. 61° (18 mm); n_D^{20} 1.4265) and 1.8 g (0.03 mole) of glacial acetic acid was prepared in a three-necked 25-ml flask fitted with thermometer, mercury-sealed stirrer, and reflux condenser. The mixture was stirred for three hours at room temperature and no signs of reaction were observed. It was then heated at 65° for 30 hours (until the sharp odor of acetic acid disappeared). Vacuum distillation then gave the following fractions:

Fraction I. b.p. 25-95° (13 mm); n_D^{20} 1. 3820; 0.7 g

Fraction II. b.p. 96-101° (13 mm); n_D^{20} 1.4212; 0.8 g

Fraction III. b.p. 102-104° (13 mm); n_D^{20} 1.4219; 3.5 g

Residue in still, b.p. 104° (13 mm); n_D^{20} 1.4335; 1.4 g

Fraction I was not investigated. Redistillation of Fractions II and III gave 3.9 g (59.5%) of a substance having b.p. 92-93° (8 mm); n_D^{20} 1.4218; d_4^{20} 0.9027; found MR 61.44; calc. for $C_{10}H_{22}SiO_3$ MR 61.60.

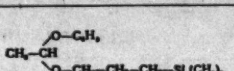
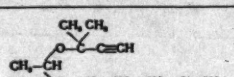
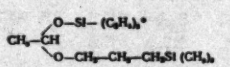
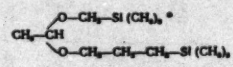
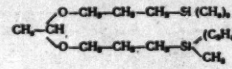
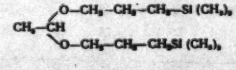
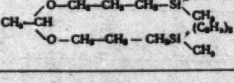
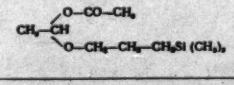
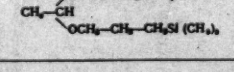
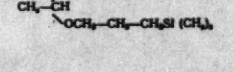
Found %: C 55.36; 55.27; H 10.35; 10.34; Si 12.61; 12.84 $C_{10}H_{22}SiO_3$. Calculated %: C 54.97; H 10.11; Si 12.85

TABLE 1

Physicochemical Constants of the Products

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calc.	Analysis C (%) found	C (%) calc.	H (%) found	H (%) calc.	Si (%) found	Si (%) calc.	Yield (%)
$(C_6H_5)_2Si(CH_3)-CH_2-CH_2-CH_2OH$	102—103 (12) 96 (10)	1.4452	0.8489	50.28	50.35	60.24 60.18	59.94	12.52 12.74	12.57	18.29 18.49	17.5	42
$(C_6H_5)_2Si(CH_3)-CH_2-CH_2-CH_2-O-CH_2-CH=CH_2$	82—83 (8)	1.4415	0.8326	59.80	59.36	64.05 64.20	64.45	12.11 11.94	11.90	15.80 15.98	15.06	68
$CH_2(OC_6H_5)-CH(OH)-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2$	102 (10)	1.4253	0.8420	70.62	70.86	62.11 62.34	62.01	11.96 12.08	12.10	11.43 11.49	12.07	68.2
$CH_2(O-C(CH_3)_2-C\equiv CH)-CH(OH)-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2$	105—107 (7.5)	1.4319	0.8580	74.44	73.88	64.32 64.55	64.41	10.90 10.84	10.81	10.53 10.72	11.57	56
$CH_2(O-CH_2-CH_2-CH_2-Si(CH_3)_2)-CH(O-CH_2-CH_2-CH_2-Si(CH_3)_2)-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2(C_6H_5)$	140—141 (3)	1.4425	0.8589	98.26	99.01	59.87 59.93	60.30	12.04 11.93	12.02	17.00 17.37	17.63	61.5
$CH_2(O-CH_2-CH_2-CH_2-Si(CH_3)_2(C_6H_5))-CH(O-CH_2-CH_2-CH_2-Si(CH_3)_2(C_6H_5))-CH_2-O-CH_2-CH_2-CH_2-Si(CH_3)_2(C_6H_5)$	156—157 (2)	1.4492	0.8666	107.42	108.27	61.96 61.91	62.31	12.19 12.23	12.20	16.25 16.46	16.19	62.2
$CH_2(O-CO-CH_3)-CH(O-CH_2-CH_2-CH_2Si(CH_3)_3)-CH_2-O-CH_2-CH_2-CH_2Si(CH_3)_3$	92—93 (8)	1.4218	0.9027	61.44	61.60	55.36 55.27	54.97	10.35 10.34	10.11	12.61 12.84	12.85	59.2
$CH_2(O-COCH_2CH_3)-CH(O-CH_2-CH_2-CH_2Si(CH_3)_3)-CH_2-O-CH_2-CH_2-CH_2Si(CH_3)_3$	99—100 (7)	1.4242	0.8979	66.23	66.07	56.66 56.75	56.85	10.40 10.38	10.41	12.01 12.26	12.08	73.2
$CH_2(O-CO-CH(CH_3)_2)-CH(O-CH_2-CH_2-CH_2Si(CH_3)_3)-CH_2-O-CH_2-CH_2-CH_2Si(CH_3)_3$	110—111 (7)	1.4262	1.8935	70.51	70.86	58.36 58.22	58.48	10.56 10.44	10.64	11.48 11.50	11.40	64

TABLE 2

No.	Formula	Extent of hydrolysis (%)		
		30 minutes under usual conditions	24 hours with shaking	6 hours at the boil
1		15.90 16.50		96.63 97.41
2		13.60 13.56		97.06 98.50
3		10.29 11.16	58,07 62,93	84.57 84.68
4		5.72 6.21	52,67 54,91	63.81 64.77
5		5.38 6.09	31,01 35,40	60.39 61.48
6		3.73 4.14	21,84 26,69	40.76 41.60
7		3.26 3.92	20,38 22,93	28.93 29.96
8		40.58 41.61		100.90 101.30
9		20.65 21.53		99.60 100.81
10		15.84 18.22		100.90 101.10

* Described in a previous communication [3].

These results correspond to the acetic ester of 1-[3-(trimethylsilyl)propoxy]ethanol.

Two other organosilicon partial acylals were prepared similarly; their physicochemical constants are given in Table 1. The extent of the hydrolysis of acetals and acylals by 2% sulfuric acid under various conditions was determined by the bisulfite method [6], and the results are given in Table 2.

SUMMARY

1. The vinyl ether of 3-(diethylmethylsilyl)-1-propanol was synthesized by a modification of the Favorsky-Shostakovsky method.

2. A study was made of the reactions of the vinyl ethers of 3-(trimethylsilyl)- and 3-(diethylmethylsilyl)-1-propanol with water, organic and organosilicon alcohols, and organic acids.

3. 3-(Diethylmethylsilyl)-1-propanol, its vinyl ether, four organosilicon acetals, and three acylals were prepared for the first time.

4. It was shown that, under similar conditions, the vinyl ether of 3-(diethylmethylsilyl)-1-propanol and organosilicon acetals and acylals are hydrolyzed with greater difficulty than their organic analogs.

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BRIEF COMMUNICATIONS

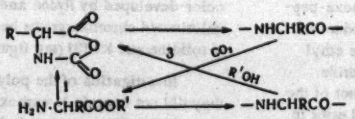
KINETICS AND CHEMISTRY OF THE POLYCONDENSATION ESTERS OF α-AMINO ACIDS

COMMUNICATION 4. COPOLYCONDENSATION OF GLYCINE ETHYL ESTER AND N-CARBOXYGLYCINE ANHYDRIDE

K.T. Poroshin, T.D. Kozarenko and Yu.I. Khurgin

The condensation of anhydrides of α-(carboxyamino) acids with esters of amino acids was applied by Wessely and Sigmund [1] and Bailey [2] in the preparation of di- and tri-peptides. The lowness of the yield of peptides of the required structure and the formation of by-products (piperazinediones and higher peptides) considerably limited the extension of this method.

In our investigation we have carried out the copolycondensation of glycine ethyl ester and N-carboxyglycine anhydride, in which we expected that a process of mutual initiation would occur. The primary process (1) is initiation of the breakdown of the anhydride of the α-(carboxyamino) acid by the amino group of the corresponding amino acid. The formation of a peptide chain by reaction of the anhydride of the carboxyamino acid is accompanied by liberation of carbon dioxide, which acts as an initiator for the polycondensation of the ester of the amino acid (2). Process 2 is accompanied by liberation of alcohol, which forms a second initiator for the polycondensation of the anhydride of N-carboxyglycine (3). Copolymerization is characterized by increase in the concentration of initiators and can therefore be regarded as an autocatalytic process. The scheme of mutual initiation can be represented as follows:

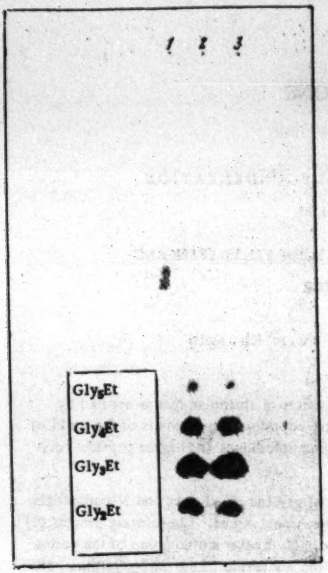


We investigated the chemical compositions of copolycondensation products obtained under identical conditions of temperature (40° for four hours) with different relative concentrations of glycine ethyl ester and N-carboxyglycine anhydride, which will be expressed as ratios of molar concentrations of anhydride and ester (A/E). Chromatographic investigation of the copolycondensation products showed that peptide esters were formed in the course of the reaction, but no free peptides were detected, which suggests that the peptide chain grows at the amino end.

EXPERIMENTAL

The copolycondensation of glycine ethyl ester and N-carboxyglycine anhydride was carried out both in the mass — by dissolving the appropriate proportion of one monomer in the other — and also in dry dioxane solution. For reaction in the mass the reaction vessel was kept in a thermostat at 40 ± 0.1° for four hours, and for copolycondensation in solution reaction was for 12 hours at the same temperature.

Mass copolycondensation was carried out for values of A/E of 0.02, 0.04, 0.067, 0.08, 0.168 and 0.233, and



Chromatographic separation on paper of products of the copolycondensation of glycine ethyl ester and N-carboxyglycine anhydride in the system butyl alcohol + acetic acid + water (4 : 1 : 5) after threefold development: 1) mixture of glycine and the di-, tri-, tetra-, penta- and hexa-peptides of the glycine series; 2) product of the copolycondensation of glycine ethyl ester and N-carboxyglycine anhydride (A/E 0.08; 40°; 4 hours); 3) product of the polycondensation of glycine ethyl ester in presence of CO_2 [3] (CO_2/E 0.08; 40°; 4 hours).

for solution copolymerization the ratios were 0.1, 0.25, 0.45, 0.66, 1.0, 1.5, 2.0, 3.0 and 9.0.

At the end of reaction in the mass, the reaction mixture was cooled, and the solid part was ground with dry ether, filtered off, and again washed with ether.

The reaction products from the solution-copolymerization reaction were freed from dioxane at 40° under low pressure and then treated as in the first case.

The combined filtrate was analyzed for the content of unchanged glycine ethyl ester by the method desctibed previously [3]. The same filtrate was tested for N-carboxyglycine anhydride by the method of Berger, Sela and Katchalski [4]. Chromatographic investigation of the ethereal filtrate showed that it contained glycine ethyl ester and traces of glycylglycine ethyl ester. In no case was N-carboxyglycine anhydride detected. The polymer, which contained peptide ethers of various chain lengths, was investigated by the method of differential titration developed previously [5] for the contents of triglycine esters, the "tetrapeptide" fraction, and 2,5-piperazinedione [6]. The mass-copolycondensation products were investigated by partition chromatography on paper. The chromatograms were formed in the systems butyl alcohol + acetic acid + water (4 : 1 : 5) and phenol + water (4 : 1) on chromatographic paper supplied by the Leningrad factory Goznak.

In the first sytem the peptide esters can be readily separated. Free peptides and glycine have low R_F values and are not separated in this system. No peptides or glycine were detected in the condensation products. A chromatogram was taken also by Keil's method [7], and in this also no free peptides were detected. The chromatograms were color-developed by Rydon and Smith's method [8], the chlorinated chromatograms being treated in a solution of o-tolidine and KI [9] (see figure).

Investigation of the polymers obtained showed that they did not contain N-carboxyglycine anhydride. The content of tripeptide esters varied from 10.2% to 33.6%. The content of tetrapeptide and higher peptide esters varied from 20.10% to 48.35%. Piperazinediones were present in the polymers in amounts depending on A/E and varying from 16.10% down to scarcely detectable amounts.

SUMMARY

1. Copolycondensation of N-carboxyglycine anhydride and glycine ethyl ester was carried out in the mass and in solution for various relative amounts of monomers. The chemical compositions of the products were studied.

2. Copolycondensation proceeds under conditions of mutual initiation. No N-carboxyglycine or free peptides were detected in the copolycondensation products, but peptide esters and various amounts of piperazinediones were present.

3. It is suggested that the peptide chain grows from the amino end.

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* Original Russian pagination. See C. B. Translation.

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EFFECT OF PYRIDINE ON THE RATE AND SELECTIVITY OF THE HYDROGENATION OF DIPHENYLACETYLENE AND CYCLOPENTADIENE OVER RANEY NICKEL AND PLATINUM BLACK

L.Kh. Freidlin and B.D. Polkovnikov

It is known that pyridine acts not only as a catalyst poison in hydrogenation, but effects also the selectivity of the catalyst [1-3]. Thus, in pyridine solution in presence of palladium, triple bonds are hydrogenated only as far as the double-bond stage, whereas in alcohol and dioxane, reaction proceeds to the single-bond stage [4, 5].

It was considered to be of interest to study the effect of pyridine on the activity and selectivity of another catalyst for low-temperature hydrogenation – Raney nickel. With this object, in the present investigation we made comparative measurements of the rates of hydrogenation of diphenylacetylene and cyclopentadiene over Raney nickel in 96% ethanol and the same solvent with addition of 10% of pyridine, in cyclohexane and the same solvent with addition of 10% of pyridine, and in pyridine alone. Reaction was carried out in the liquid phase in a hydrogenation flask at 25° and atmospheric pressure. The experimental conditions, which are given in the table, ensured that reaction occurred in the kinetic region. The catalyst was prepared by leaching a 50% Ni-Al alloy with 20% sodium hydroxide for two hours at 100°. Electrolytic hydrogen was used.

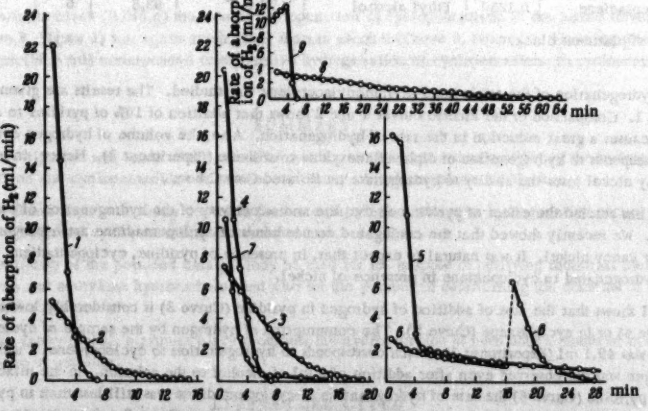

Fig. 1. Hydrogenation of cyclopentadiene (3-9) and diphenylacetylene (1-2) over Raney nickel (1-7) and platinum black (8-9): 1, 4, 9) in ethanol; 2, 7, 8) in ethanol + 10% of pyridine; 3) in pyridine; 5) in cyclohexane; 6) in cyclohexane + 10% of pyridine.

TABLE

Effect of Pyridine on the Rate and Selectivity of the Hydrogenation of Diphenylacetylene and Cyclopentadiene in Presence of Raney Nickel and Platinum Black. Experimental Conditions: weight of nickel 0.4 g; volume of solvent 10 ml; rate of agitation 900 shakes per minute; length of sweep 127 cm

No.	Substance hydrogenated	Weight of substance (g)	Solvent	Consumption of hydrogen (ml)		Duration of reaction (minutes)	
				theoretical	actual	total	half-period
1	Diphenylacetylene	0.1700	Ethyl alcohol	48.6	47.8	7	1.1
2	Diphenylacetylene	0.2000	Alcohol-pyridine	57.6	28.5	19	19
3	Cyclopentadiene	0.1266	Pyridine	97.6	49.1	19	19
4	Cyclopentadiene	0.0628	Ethyl alcohol	48.6	47.8	7	1.3
5	Cyclopentadiene	0.0618	Alcohol-pyridine	48.0	23.9	15	15
6	Cyclopentadiene	0.1255	Cyclohexane-pyridine	94.0	45.8	28	28
7	Cyclopentadiene	0.1236	Cyclohexane	92.8	92.1	–	–
8	Mixture of cyclopentadiene and diphenylacetylene	0.0624 0.1699	Ethyl alcohol	48.9 49.3 } 98.2	93.7	10	1.9
9	Mixture of cyclopentadiene and diphenylacetylene	0.0628 0.1666	Alcohol-pyridine	48.7 48.1 } 96.8	48.6	32	32
10	Mixture of cyclopentadiene and diphenylacetylene	0.0620 0.1692	Cyclohexane	49.0 49.6 } 98.6	95.6	40	–
11	Mixtureof cyclopentadiene and diphenylacetylene	0.0628 0.1673	Cyclohexane-pyridine	48.7 48.1 96.8	49.0	59	59
12*	Cyclopentadiene	0.1254	Alcohol-pyridine	97.1	96.5	64	17
13*	Cyclopentadiene	0.1250	Ethyl alcohol	97.0	93.8	6	2.3

*In presence of platinum black.

First, hydrogenation of the triple bond of diphenylacetylene was studied. The results are given in the table and in Figure 1. Comparison of the kinetic curves 1 and 2 shows that addition of 10% of pyridine to alcohol or cyclohexane causes a great reduction in the rate of hydrogenation. Also, the volume of hydrogen consumed (28.5 ml) corresponds to hydrogenation of diphenylacetylene to stilbene (Experiment 2). Hence, in presence of pyridine Raney nickel loses the ability to hydrogenate an isolated C = C bond.

No one has studied the effect of pyridine on the rate and selectivity of the hydrogenation of conjugated double bonds. We recently showed that the conjugated double bonds of cyclopentadiene are hydrogenated successively over Raney nickel. It was natural to expect that, in presence of pyridine, cyclopentadiene would be selectively hydrogenated to cyclopentene in presence of nickel.

Figure 1 shows that the rate of addition of hydrogen in pyridine (Curve 3) is considerably lower than in alcohol (Curve 4) or in cyclohexane (Curve 5). The consumption of hydrogen by the sample of cyclopentadiene (0.002 mole) was 49.1 ml (Experiment 3), which corresponds to hydrogenation to cyclopentene. Further absorption of hydrogen was not observed even after addition of 5 ml of alcohol to the solution. In the mixed solvent cyclohexane-pyridine (Curve 6) the rate of hydrogenation of cyclopentadiene was still less than in pyridine. With addition of 5 ml of alcohol the reaction rate increased greatly, and on Curve 6 a sharp maximum appears. However, in this experiment also, cyclopentadiene was hydrogenated only as far as cyclopentene (Experiment 6). Analogous selectivity was observed in the hydrogenation of cyclopentadiene in the mixed solvent alcohol-pyridine (Curve 7, Experiment 5).

It might be expected that, over Raney nickel in presence of pyridine, a binary mixture of diphenylacetylene

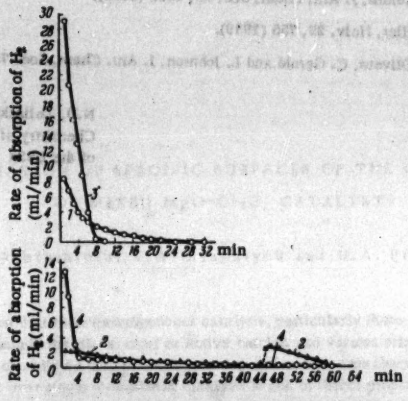

Fig. 2. Hydrogenation of mixtures of cyclopentadiene and diphenylacetylene: 1) in alcohol + 10% pyridine; 2) in cyclohexane + 10% pyridine; 3) in alcohol; 4) in cyclohexane.

and cyclopentadiene would also be hydrogenated selectively, i.e., to a mixture of stilbene and cyclopentene. Judging from the consumption of hydrogen, this expectation is fully realized. The kinetic curves for the hydrogenation of binary mixtures are given in Figure 2. It will be seen that, in the mixed solvents alcohol-pyridine (Curve 1) and cyclohexane-pyridine (Curve 2), the rate of reaction is considerably lower than in alcohol (Curve 3) or in cyclohexane (Curve 4). The consumption of hydrogen in absence of pyridine (Experiments 8 and 10) is twice as great as in presence of pyridine (Experiments 9 and 11).

Over platinum black (0.046 g) the rate of hydrogenation of cyclopentadiene in the mixed solvent alcohol-pyridine (Curve 8, Figure 1) was again much lower than in alcohol (Curve 9, Figure 1). However, the consumption of hydrogen (96.5 ml) corresponded to exhaustive hydrogenation of cyclopentadiene to cyclopentane (Experiment 12).

SUMMARY

1. An investigation was made of the effect of pyridine on the rate and selectivity of the hydrogenation of diphenylacetylene and cyclopentadiene in presence of Raney nickel and platinum black.

2. It was found that, over Raney nickel in presence of pyridine, selective hydrogenation occurs: diphenylacetylene to stilbene and cyclopentadiene to cyclopentene.

This specificity of the poisoned catalyst may be used for the purpose of purifying industrial olefin fractions from diene and acetylene hydrocarbons, and also for the purpose of determining the contents of the latter in ethylenic hydrocarbons.

3. Unlike Raney nickel, platinum black promotes the hydrogenation of both double bonds of cyclopentadiene in presence of pyridine.

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DETERMINATION OF SPECIFIC SURFACES OF THE COMPONENTS OF MIXED $MgO-Cr_2O_3$ CATALYSTS

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It is generally known that most heterogeneous catalysts, particularly those of practical importance, are mixed catalysts, which include metals on inert or active carriers and various mixtures of oxides and other compounds. It has long been established that between activity and surface area there exists a relationship, which for some simple reactions over single-component catalysts is one of direct proportionality [1]. The specific surface has therefore become one of the most important characteristics of catalysts. Methods of determining specific surface from the adsorption isotherms of inert gases or organic vapors have been fairly fully developed. These methods, however, being based on physical adsorption, give the total surface of simple or mixed catalysts, whereas for mixed catalysts it is particularly important and interesting to know what fraction of the surface is contributed by each of the components.

To solve this problem the physical adsorption method must be combined with the measurement of specific chemisorption. This method of determining the specific surfaces of the components of binary catalysts has been applied in very few cases and, with one exception, only for metal-carrier systems, the total surface being most frequently determined from low-temperature adsorption of nitrogen, and the metal surface from data on the chemisorption of hydrogen (Pt) or of CO (Ni, Co, Fe). We are here referring to the determination of the surface of Pt in platinized charcoal [2-4], Co on kieselguhr [5], Ni on alumina [6], Pt on barium sulfate [7] and on silica [8], and Fe in the promoted catalyst for ammonia synthesis [9]. The above-mentioned exception, in which the surface occupied by an oxide was measured, is the determination of the distribution of the promoter (K_2O) in the iron catalyst for ammonia synthesis by measuring the physical adsorption and chemisorption of CO_2 [10]. These examples cover all the information in the literature of catalysis on the separate determination of the surfaces of the components of mixed catalysts.

These results enable us to conclude that the determination of the specific surface of reduced metal in a mixed catalyst by the method discussed does not present any substantial difficulties. This, however, cannot be said of oxide mixtures – not only the more complex ones, but even binary mixtures. Not a single example of such systems has been treated in the literature, but this is not because the problems are not of interest, but because it is extremely difficult to find a substance which, under some conditions or other, will be chemisorbed by only one of the components of a mixed catalyst. In our investigation, however, we have been able to find such a substance.

EXPERIMENTAL

By determining the specific surfaces of catalysts from adsorption isotherms of benzene vapor in a flow system at ordinary pressure [11] and comparing the results for binary catalysts based on magnesia with specific surfaces determined from the chemisorption of iodine from carbon tetrachloride solution [12], we found the system $MgO-Cr_2O_3$, in which only one component (MgO) chemisorbs iodine. We then carried out experiments on the separate determination of the specific surfaces of the components of this catalyst, and we prepared a series of catalysts with varying contents of the components. Some of these were prepared by coprecipitation with 10% ammonia from mixed solutions of magnesium and chromium nitrates at room temperature. The precipitate was washed, molded, dried at 110-120°, and calcined in the air at 425° for six hours for the conversion of hydroxides into oxides. Pure MgO and Cr_2O_3 were prepared similarly. Three catalysts were prepared by impregnating

TABLE

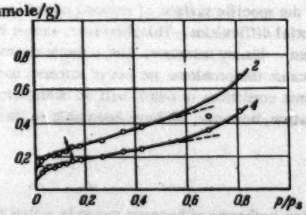
Catalyst	Composition (mole %)		S	S_I	S_{MgO}	$S_{Cr_2O_3}$	Method of preparation
	Cr_2O_3	MgO	(sq. m/g)				
1	0	100	—	35	35	—	Precipitation
2	5	95	60	25	25	35	Coprecipitation
3	5	95	43	23	23	20	Impregnation
4	10	90	41	21	21	20	Impregnation
5	20	80	48	12	12	36	Impregnation
6	90	10	81	46	46	35	Coprecipitation
7	95	5	79	25	25	54	Coprecipitation
8	99	1	38	5	5	33	Coprecipitation
9	100	0	32	0	—	32	Precipitation

molded MgO with various amounts of chromium nitrate solution and then heating to effect thermal decomposition.

We described the procedure for determining specific surface by adsorption of benzene vapor in a flow system in a previous paper [11]. The determination of surface from the chemisorption of iodine by MgO catalysts [12] was carried out as follows. About one gram of catalyst was weighed accurately and transferred to a 200-ml flask with a ground stopper; 25 ml of 0.1 N iodine in CCl_4 was added, and the mixture was allowed to stand for 2.5 hours in the dark. The clear liquid, not containing any suspended particles of catalyst, was poured off carefully, and 10 ml was transferred to a flask; 15 ml of alcoholic KI (2 g of KI in 300 ml of C_2H_5OH and 84 ml of H_2O) was added, and the mixture was titrated with 1.0 N thiosulfate; no indicator was necessary. A control experiment was carried out with iodine solution without catalyst. The determination was repeated on several test samples of the same catalyst. The value of the specific surface, which is equal to the iodine value [12], was calculated from the formula:

$$S_I = \frac{a \cdot 2.5 \cdot T_{Na_2S_2O_3}}{A},$$

in which a is the difference between the volumes of thiosulfate solution required in the working and control titrations, $T_{Na_2S_2O_3}$ is the titer of the thiosulfate solution, and A is the weight of catalyst (g). Comparison of the values obtained by this method with those obtained from nitrogen adsorption isotherms [12] and from benzene vapor adsorption isotherms [11] showed close agreement of results.



By way of example we show the adsorption isotherms for benzene vapor on Catalysts 2 and 4 (see figure). The table gives the compositions and methods of preparation of the catalysts, the specific surfaces found by chemisorption of iodine (S_I) and from adsorption isotherms of benzene vapor (S), and also the specific surface contributed by each of the components of the catalyst (S with the appropriate subscript). These data show that Cr_2O_3, for which S = 32 sq. m/g, does not chemisorb iodine to an appreciable extent, so that its surface is not determined by the iodine method. On the basis of this observation we may suppose that adsorption of iodine under the given conditions makes it possible to determine the specific surface of magnesia, and $S - S_I$ will give the specific surface of Cr_2O_3 in the catalyst. As will be seen from the table, for all the mixed catalysts S_I is indeed less than S, and with increase of the proportion of Cr_2O_3 in the mixture it falls continuously, both in the impregnated and in the coprecipitated catalysts.

For the correct appraisal of the results it is important to note that they cannot depend on the character of the porosity since the area occupied by an iodine molecule on the catalyst surface (21 A^2 [12]) is less than the area occupied by a benzene molecule, which various data in the literature indicate to be 40 A^2. It is therefore impossible to explain the fact that S_I is less than S by the hypothesis that some of the pores are inaccessible to

iodine molecules, for iodine molecules are smaller than benzene molecules. The only explanation of the difference between S and S_I is that only part of the surface adsorbs iodine and this part is formed of MgO.

The data in the table show that impregnated catalysts have a lower S than precipitated, which is quite understandable in view of the mutual protective action from crystallization and sintering found in coprecipitated catalysts. Although this effect was absent in the impregnated catalysts, the value of S was greater than that of the original MgO as a result of the introduction of the second component.

Hence, a combination of the methods of chemisorption of iodine and of adsorption of benzene vapor enabled us to determine separately the specific surfaces of the components of a mixed oxide catalyst. We have shown previously that, apart from MgO, many oxides chemisorb iodine from its solution in CCl_4 [11]. We therefore consider our present results to be interesting in connection with the possibility of determining not only the total specific surface, but also the specific surface of Cr_2O_3 in various mixed catalysts containing other oxides instead of magnesia.

SUMMARY

A method is proposed for the separate determination of the specific surfaces of the components of MgO-Cr_2O_3 catalysts by a combination of two methods of determining specific surfaces: from isotherms for the physical adsorption of a vapor (benzene) and from the chemisorption of iodine from its solution in carbon tetrachloride.

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SYNTHESIS OF C^{14}-LABELED TOLUENE

A.A. Korotkov and S.P. Mitsengendler

Several methods have been proposed for the synthesis of C^{14}-labeled toluene, and these consist of 3-4 stages and give yields of 30-50% on the original active preparation [1, 2]. It is clear that for this purpose we may use the method of methylation of benzene and its derivatives. In the methylation of benzene with dimethyl sulfate and other alkylating agents in presence of aluminum chloride, the yield of toluene, which is diluted with a large excess of benzene, is comparatively low (59% [3] and 32% [4]). In the methylation of bromobenzene (via phenylmagnesium bromide) with dimethyl sulfate, an excess of the latter is required and the yield of toluene does not exceed 41% on the amount of bromobenzene taken [5]. In the methylation of bromobenzene with methyl iodide in presence of sodium [6], equimolecular amounts of reactants are used, but the authors do not state the yield of toluene. We selected this method for the preparation of C^{14}-labeled toluene.

EXPERIMENTAL

1. Preparation of C^{14}-labeled Methyl Iodide. This was prepared from C^{14}-labeled methanol and hydriodic acid. With minor modifications, the microapparatus used for the preparation of methyl iodide from methyl formate (see figure) [7] was used for the synthesis.

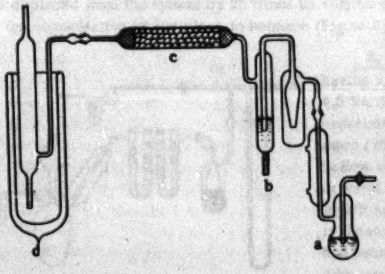

Diagram of microapparatus for the preparation of methyl-C^{14} iodide: a) reaction flask; b) aqueous suspension of red phosphorus; c) calcium chloride tube; d) trap for the condensation of methyl-C^{14} iodide.

Methanol-C^{14} (0.3 g) was cooled to −70° and dissolved in 10 ml of hydriodic acid of sp. gr. 1.7. The solution was poured into the flask a. A feeble current of nitrogen was passed continuously through the reaction mixture, which was heated gradually in an oil bath so that it reached a temperature of 130° in 90 minutes. The methyl-C^{14} iodide formed was carried away by the current of nitrogen (condenser not in operation) and condensed in the trap d, which was cooled to −70°. The yield of methyl-C^{14} iodide was 85-90% on the amount of alcohol taken.

2. Alkylation of Bromobenzene with Methyl-C^{14} Iodide. A solution of 13.56 g (0.095 mole) of methyl-C^{14} iodide and 22.54 g (0.14 mole) of bromobenzene in 20 ml of ether was cooled and rapidly poured into a flask containing 8 g of sodium wire in 10 ml of ether. The flask was connected through a condenser to a trap surrounded by a cooling mixture (−70°) contained in a Dewar vessel. Reaction began after the mixture had been heated slowly (over 1-2 hours) to a feeble boil, and it came to an end after 6-8 hours. Gentle reaction was maintained by cooling the flask with water. The mixture was allowed to stand overnight, and ether, unchanged methyl-C^{14} iodide (fraction boiling up to 50°), and a wide fraction boiling up to 130° were distilled off.

Pure toluene (3-5 ml) was added to the dry residue, and this was distilled into the receiver containing the wide fraction. The total toluene-containing distillate was boiled for 3-4 hours with sodium and then fractionated

through a microcolumn.

From the original methyl-C^{14} iodide, total activity 165 microcuries, we obtained unchanged methyl-C^{14} iodide, activity 13.9 microcuries, and 21.35 g of toluene-C^{14}, activity 131.5 microcuries. The yield of toluene-C^{14} was therefore 80% on the original amount of methyl-C^{14} iodide and 87% on the amount that reacted. The constants of the toluene-C^{14} obtained: b.p. 109-110° (753 mm), d_4^{20} 0.8654; n_D^{20} 1.4967.

The activity measurements were made with a "B" apparatus with end-on counter.

Senior laboratory worker V.D. Prochukhan took part in the experimental work.

SUMMARY

C^{14}-labeled toluene was synthesized by the alkylation of bromobenzene with methyl-C^{14} iodide. The yield of toluene-C^{14} was 80% on the original amount of methyl-C^{14} iodide and 87% on the amount that reacted.

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SYNTHESIS OF C^{14}-LABELED BENZENE

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Several methods have been published for the preparation of benzene-C^{14} [1-3]. With the exception of Turner's method [3], these methods give comparatively low yields – 22-25% on the original amount of active carbon. For the synthesis of benzene-C^{14} we used the known reaction of condensation of acetylene to benzene [4-6], by which it is possible to obtain benzene-C^{14} in one stage. The most satisfactory method of carrying out this reaction was found to be Berl and Hofmann's method [5], in which 98-99% of the acetylene is utilized in the formation of an aromatic tar containing up to 40% of a benzene fraction.* The method consists in the passage of acetylene diluted with steam at high speed through a tube containing porcelain beads at 740°. The steam has the purpose of facilitating the removal of heat and so minimizing the destruction of the condensation products first formed and reducing coke formation.

EXPERIMENTAL

1. Preparation of Acetylene-C^{14}. Acetylene-C^{14} was prepared according to the scheme: $BaCO_3^* \rightarrow BaC_2^* \rightarrow H_2C_2^*$: barium carbide by the method developed by Keier [7]; and acetylene by decomposition of the carbide with water in the apparatus described by Cheronis [8], as modified in detail by us** (Figure 1). By this method the yield of acetylene was 72-80% on the amount of barium carbonate taken. The labeled acetylene (16-20 ml) was displaced from the system by 25 times its volume of acetylene-C^{12} into one of the gas burets of the apparatus for the condensation of acetylene to benzene (Figure 2).

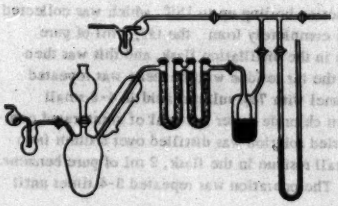

Fig. 1.

2. Condensation of Acetylene-C^{14}. Acetylene-C^{14} (500 ml) having a total activity of 0.615 millicurie was passed at a rate of 4.5 liters/hour from the gas buret 1 through two successive vessels containing water in the water thermostat 4. Constancy of temperature (78 ± 0.5°) was attained by the use of boiling ethanol in the hollow walls of the thermostat. The gas mixture, containing 45% of water vapor, passed on to a quartz tube 5 (diameter 15 mm, length and volume of heated part 160 mm and 28 ml, respectively) heated to 740° and filled with 4-mm beads of white clay that had been fired at 1200°. The upper, entering end of the reaction tube was heated to 300° with an electric tube furnace, length 50 mm. The tar and steam condensed in the receiver 6 at −5° and in three successive traps at −15°.

The gas mixture (250 ml), consisting mainly of unchanged acetylene, passed to gas buret 2. In one cycle about 60% of the acetylene reacted. The gas mixture passing into the gas buret 2 was diluted to 500 ml with acetylene-C^{12} from the gas buret 3, and was again passed through the reactor. In this case the gas buret 1 served as a receiver for unchanged acetylene.

*Berl and Hofmann carried out the condensation of acetylene in a large apparatus capable of passing 60 liters of acetylene per hour. The authors did not isolate benzene and toluene from the fractions obtained.

**The wire-filled U-shaped trap for condensation of acetylene was replaced by a more compact bell-shaped trap in an aluminum jacket. The yield of acetylene was determined by the pressure change in the system.

Each cycle lasted 5-7 minutes. In the course of 11 cycles the acetylene-C^{14} reacted almost completely, the total consumption of acetylene being 2-3 liters (2.44 g). From this amount of acetylene about 2.5 ml (2.35 g) of an aromatic C^{14} tar was obtained (8% of the acetylene was consumed in the formation of coke and gaseous saturated hydrocarbons). In the course of the experiment, which lasted 65-70 minutes, only a very little coke was formed: it formed a thin covering on the beads and the walls of the quartz tube.

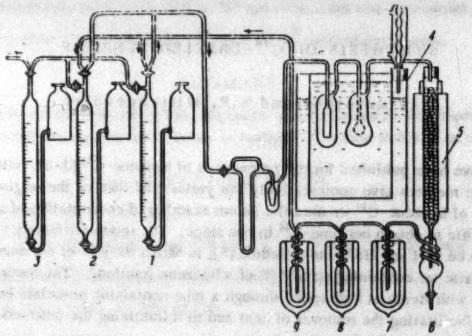

Fig. 2.

This acetylene condensation process was first tried out on acetylene-C^{12}. In this case the yield of tar was also 95-96%. For the determination of the yield and purity of the benzene, a fraction boiling up to 150° was distilled from the tar, purified from unsaturated compounds, and then fractionated through a microcolumn. From 13.3 g of the fraction (48%), 9.82 g of benzene was obtained (33.6% yield on the amount of acetylene taken). Apart from benzene, some toluene was isolated (3.2% yield on the amount of acetylene taken).* The constants of the benzene obtained were: b.p. 80° (757 mm); d_4^{20} 0.8771; n_D^{18} 1.5013.

3. Isolation of Benzene-C^{14} and Toluene-C^{14} from the Tar Obtained. After the experiment the reactor and trap were washed out with ether and the resulting solution was fractionated from a flask having a small Vigreux column (height 100 mm). Ether came over first, and then a fraction boiling up to 150°, which was collected in a small separating funnel. In order to separate benzene-C^{14} more completely from the tar, 2 ml of pure benzene, free from unsaturated compounds, was added to the residue in the distillation flask, and this was then distilled into the same separating funnel. The operation of washing the tar residue with benzene was repeated three times. The distillate was treated directly in the separating funnel with 75% sulfuric acid in 4-5 small portions. It was then washed with water and dried with fused calcium chloride (after removal of unsaturated compounds the hydrocarbon layer was reduced by 5% in volume). The dried solution was distilled over sodium from a flask having a small Vigreux column (height 100 mm). To the small residue in the flask, 2 ml of pure benzene was added, and this was distilled into the receiver for benzene-C^{14}. The operation was repeated 3-4 times until C^{14} was absent in the distillate.**

From the original acetylene-C^{14}, total activity 0.615 millicurie, 18.2 g of benzene-C^{14} was obtained, activity 0.183 millicurie, i.e., the yield of benzene-C^{14} was 29.8% on the amount of active carbon in the acetylene-C^{14} taken. The residue from the distillation of benzene was diluted with 1 ml of toluene, free from unsaturated compounds, and was distilled. The operation was repeated until C^{14} was absent in the distillate. We obtained 2.26 g of toluene having a total activity of 0.0078 millicurie, which corresponds to 1.26% on the amount of active carbon in the acetylene taken.

Laboratory worker A.P. Kudryavtsev took part in the experimental work.

*In Zelinsky's method [4] the yields of benzene and toluene are 23-25% and 4%, respectively.

**The activities of the preparations obtained were measured with a "B" apparatus with end-on counter.

SUMMARY

C^{14}-labeled benzene was synthesized by the condensation of acetylene-C^{14} diluted with steam at 740°, the time of contact being 3.5 seconds. The yield of benzene-C^{14} was 30% on the amount of active carbon taken.

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ORGANOBORON COMPOUNDS

COMMUNICATION 14.* ACTION OF ORGANIC BASES ON CHLORODIPHENYLBORINE

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The reaction between esters of organoboron acids and phosphorus pentachloride provides a simple method of preparing organic monochloroborines (I) [3,4] and dichloroborines (II) [5], and also a new type of boron compounds, the chloro esters RBCl·OR' (III) [4,6].

$$R_2BOR' + PCl_5 = R_2BCl + POCl_3 + R'Cl.$$
(I)

$$RB(OR')_2 + 2PCl_5 = RBCl_2 + 2POCl_3 + 2R'Cl.$$
(II)

$$RB(OR')_2 + PCl_5 = RB\begin{matrix}Cl\\OR'\end{matrix} + POCl_3 + R'Cl.$$
(III)

Hence, organic chloroborines are very readily accessible compounds, which is a prerequisite for the study of their chemical properties and their use for synthesis of organoboron compounds.

The present paper gives the results of an investigation of the reactions of chlorodiphenylborine, prepared by the action of phosphorus pentachloride on diphenylborinic ester in presence of organic bases.

When treated with two equivalents of diethylamine in ethereal solution, there is a lively reaction accompanied by boiling of the ether. The products are (diethylamino)diphenylborine (IV) and diethylamine hydrochloride:

$$(C_6H_5)_2BCl + 2(C_2H_5)_2NH = (C_6H_5)_2B-N(C_2H_5)_2 + (C_2H_5)_2NH\cdot HCl.$$
(IV)

Piperidine reacts similarly with chlorodiphenylborine and gives diphenylpiperidinoborine (V):

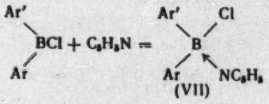
$$(C_6H_5)_2BCl + 2C_5H_{11}N = (C_6H_5)_2B-NC_5H_{10} + C_5H_{11}N\cdot HCl.$$
(V)

In the reaction of ammonia with an ethereal solution of chlorodiphenylborine at room temperature, chlorine is not replaced by an amino group as it is in the case of secondary amines, but ammonia adds with formation of a chlorodiphenylborine-ammonia complex (VI):

$$(C_6H_5)_2BCl + NH_3 = (C_6H_5)_2B\begin{matrix}Cl\\\leftarrow NH_3\end{matrix}$$
(VI)

Chlorodiphenylborine can also form a stable complex compound with pyridine, and stable complexes with pyridine are formed also be chloro-p-chlorophenylphenylborine and by chlorodi-1-naphthylborine (VII):

*Communication 11, see [1]; Communication 13, see [2].



(VII)

in which Ar = C_6H_5 or 1-$C_{10}H_7$, and Ar' = p-ClC_6H_4.

EXPERIMENTAL

1. (Diethylamino)diphenylborine. A mixture of 6.4 g (0.032 mole) of chlorodiphenylborine [3] and 25 ml of dry ether was prepared in a three-necked flask fitted with reflux condenser, tube for the passage of nitrogen, and dropping funnel. The mixture was stirred while 4.7 g (0.064 mole) of diethylamine diluted with 10 ml of dry ether was added slowly. The ether came to the boil, and a colorless finely crystalline precipitate formed. The crystals were filtered off and washed with 20 ml of dry ether. The product was 3.53 g of diethylamine hydrochloride, m.p. 225-226°, undepressed by admixture of known diethylamine hydrochloride. Ether was distilled from the filtrate, and vacuum distillation of the residue in a current of nitrogen gave 5.47 g of (diethylamino)diphenylborine (71.5% yield), b.p. 159-162° (11 mm) and d_4^{20} 0.9953.

Found %: C 80.95; H 8.46; B 4.60. $C_{16}H_{20}BN$. Calculated %: C 81.07; H 8.44; B 4.56.

(Diethylamino)diphenylborine is a colorless substance which crystallizes when cooled; m.p. 36-37°. It very readily oxidizes in the air. It is readily soluble in acetone, alcohol and ether.

2. Diphenylpiperidinoborine. An ethereal solution of 5 g (0.059 mole) of piperidine was added slowly to a stirred solution of 5.3 g (0.026 mole) of chlorodiphenylborine in 10 ml of ether. The precipitate of piperidine hydrochloride (3.34 g, m.p. 246°) was filtered off. The substance showed no depression of melting point in admixture with a known sample of piperidine hydrochloride. Solvent was distilled from the filtrate, and vacuum distillation of the residue in a current of nitrogen gave 3.5 g (53%) of diphenylpiperidinoborine, b.p. 200-203° (14 mm).

Found %: C 82.09; H 7.96; B 4.35. $C_{17}H_{20}BN$. Calculated %: C 81.98; H 8.03; B 4.34.

Diphenylpiperidinoborine comes over as a thick colorless oil which crystallizes on standing; m.p. 65-66°. It is oxidized in the air.

3. Chlorodiphenylborine-Ammonia Complex. A stream of dry ammonia was passed through an ethereal solution of chlorodiphenylborine (1 g in 20 ml of ether). The colorless crystalline precipitate was filtered off and washed with ether. The product, amounting to 1.14 g (99%), was the chlorodiphenylborine-ammonia complex; it softens at 175-180° and does not melt completely up to 250° (in a sealed capillary).

Found %: B 4.79; Cl 15.93; Ar 71.08. $C_{12}H_{13}BNCl$. Calculated %: B 4.98; Cl 16.29; Ar 70.86.

The substance is readily soluble in alcohol, but poorly soluble in ether, acetone, benzene and chloroform.

4. Chlorodiphenylborine-Pyridine Complex. A solution of 0.88 g of pyridine in 10 ml of ether was added to a solution of 2.22 g of chlorodiphenylborine in 10 ml of ether. The colorless crystalline precipitate was filtered off and washed with ether. The product, amounting to 2.34 g (75.7%) was the chlorodiphenylborine-pyridine complex, m.p. 135-138°.

Found %: B 3.86; Cl 12.83. $C_{17}H_{15}BNCl$. Calculated %: B 3.87; Cl 12.69.

The pyridine complex is sparingly soluble in ether, acetone and benzene, and is readily hydrolyzed by atmospheric moisture.

5. Chloro-p-chlorophenylphenylborine-Pyridine Complex. A solution of 1.25 g of pyridine in 10 ml of ether was added to a solution of 1.55 g of chloro-p-chlorophenylphenylborine (prepared by the action of PCl_5

on isobutyl p-chlorophenylphenylborinate) in 20 ml of ether. The solvent came to the boil, and a precipitate of the pyridine complex of chloro-p-chlorophenylphenylborine formed. The substance was filtered off and washed with ether. The yield of pyridine complex, m.p. 130-132°, was 1.54 g (74.8%).

Found %: C 64.95; H 4.92; B 3.33; N 4.38; Cl* 11.12.
$C_{17}H_{14}BNCl_2$. Calculated %: C 65.04; H 4.81; B 3.44; N 4.46; Cl 11.31.

The substance is sparingly soluble in ether, acetone and benzene, and is readily hydrolyzed by atmospheric moisture.

6. Chlorodi-1-naphthylborine-Pyridine Complex. An ethereal solution of 1.5 g of pyridine was added to an ethereal solution of 1.59 g of chlorodi-1-naphthylborine [3]. The precipitate formed was filtered off and washed with ether. The yield of the pyridine complex of chlorodi-1-naphthylborine, m.p. 243-245°, was 1.5 g (75.3%).

Found %: B 2.74; Cl 9.19. $C_{26}H_{19}BNCl$. Calculated %: B 2.74; Cl 9.35.

The substance is sparingly soluble in organic solvents and is readily hydrolyzed by atmospheric moisture.

SUMMARY

1. By reaction with diethylamine or piperidine, chlorodiphenylborine gives (diethylamino)diphenylborine or diphenylpiperidinoborine, respectively.

2. Chlorodiphenylborine reacts with ammonia at room temperature with formation of a chlorodiphenylborine-ammonia complex.

3. Diarylchloroborines from stable complex compounds with pyridine.

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* The readily hydrolyzable boron-attached chlorine.
** Original Russian pagination. See C. B. Translation.